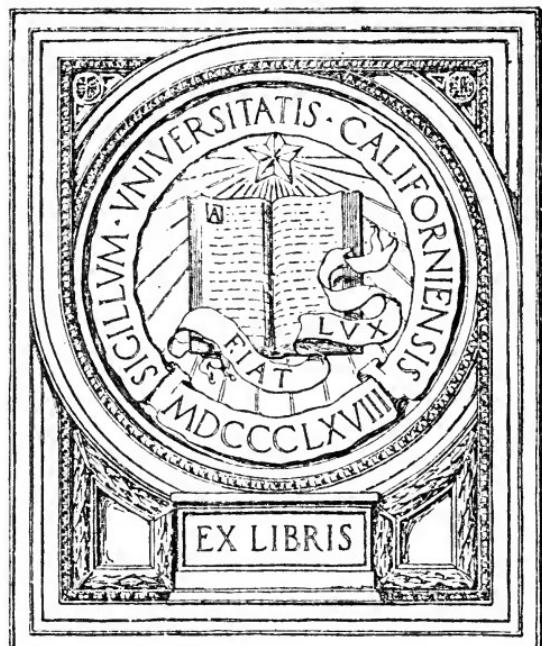


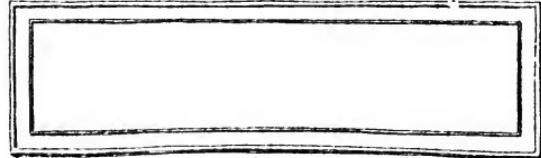
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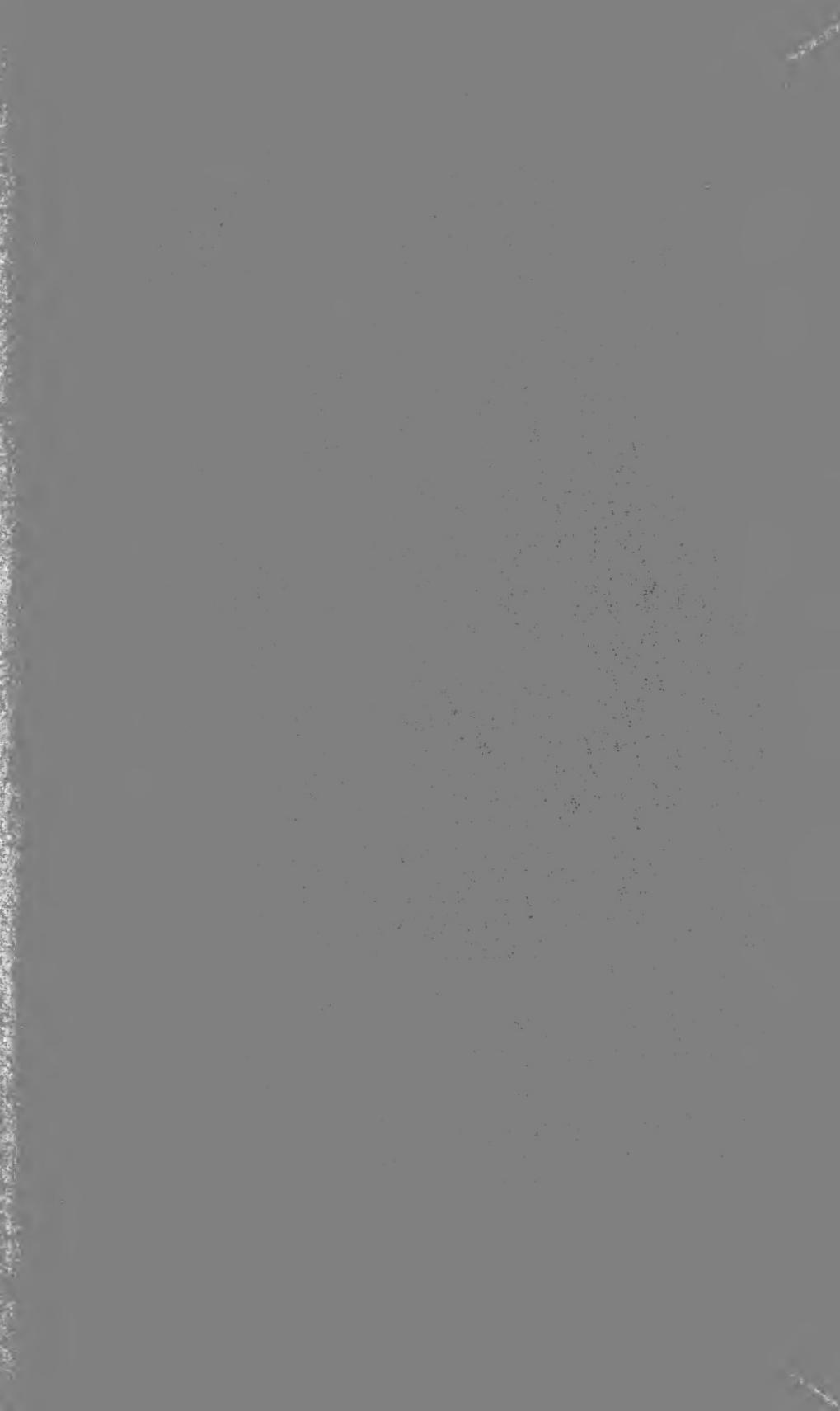


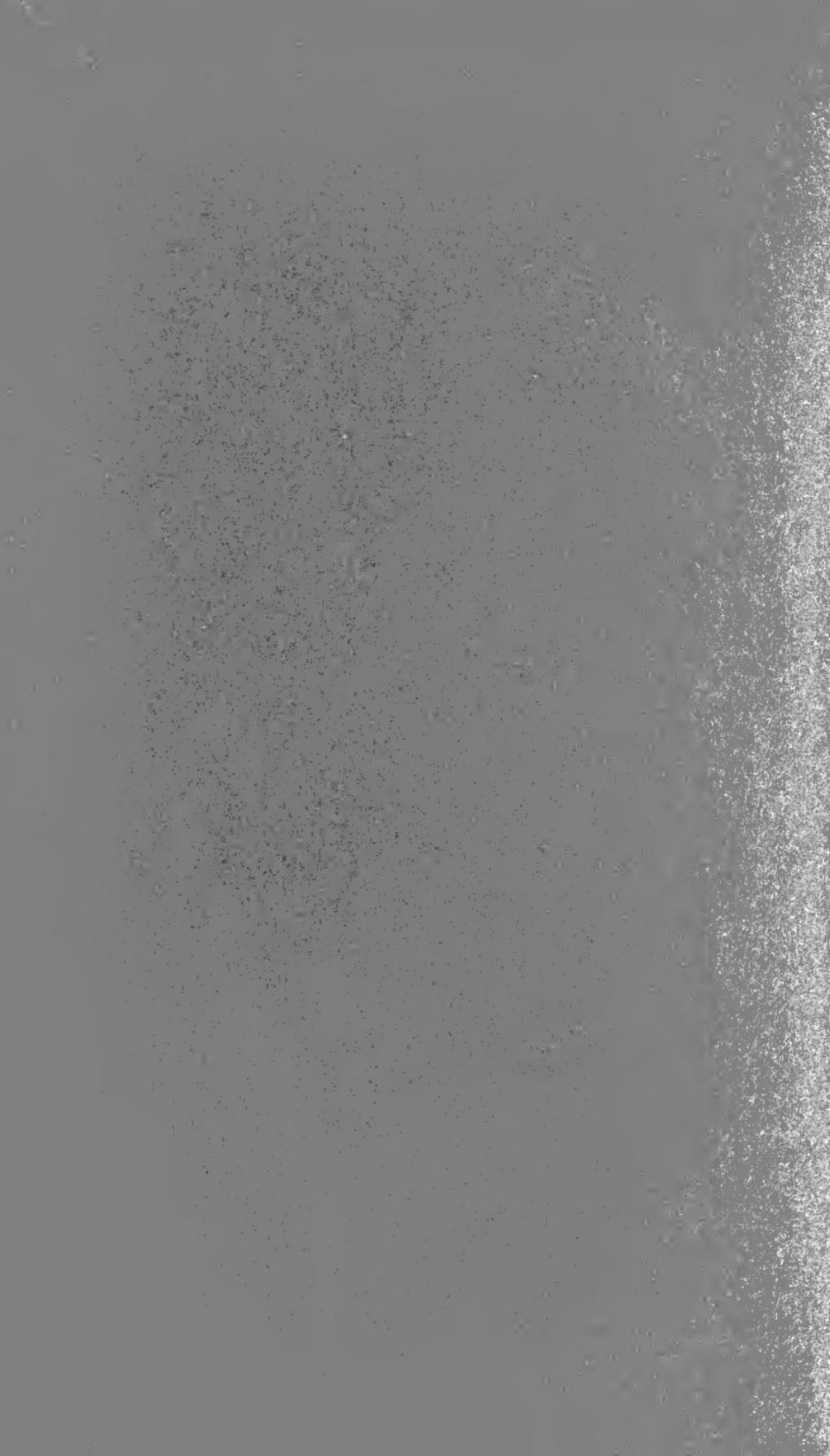
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# •PHOTO-ELECTRICITY•

BY

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## PREFACE

SINCE the account of the photo-electric effect given by R. Ladenburg in the *Jahrbuch für Radioaktivität* for 1909, no complete resumé of the subject has been written. During the past five years, however, considerable progress has been made, and it is therefore thought desirable to give some account of the condition of the subject at the present time. Such an account is attempted in this book, all forms of ionisation by light being considered, whether in solids, liquids or gases.

The photo-electric effect is regarded as a form of ionisation by light and my original intention was to use the latter expression as the title of the book. But this title suggests perhaps not so much the study of the emission of electricity from illuminated surfaces among other phenomena, as a study merely of ionisation of gases; and as most of our information as to ionisation by light has been obtained from a study of the photo-electric effect in solids and liquids, it was thought that the title "Photo-Electricity" would be more suggestive of the contents of the book.

I wish to express my best thanks to Mr T. G. Bedford, the Editor of the Cambridge Physical Series, for many valuable suggestions and for help in the revision of the proofs.

A. LL. HUGHES.

HOUSTON, TEXAS.

October 1913.



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# CHAPTER I

## INTRODUCTION

THE first important observation on the action of light on the discharge of electricity from conductors was that of Hertz in 1887, who found that a spark passed between metallic terminals in air more easily when light from another spark fell on the negative terminal. This effect led to a number of investigations by Hallwachs, Elster and Geitel, and others, who found that electrified metallic conductors lost electrification when illuminated by a suitable source of light. On taking precautions to avoid spurious effects, the important result was established that the illuminated metal could lose negative, but not positive charges. If the metal were initially insulated and uncharged, then it acquired a small positive charge as a result of illumination, but the potential to which it rose did not exceed a volt. With most metals, the leak of negative electricity ceased on the interposition of a plate of glass between the source of light and the metal. As the glass absorbs the ultra-violet radiation, it was thus proved that the effect in these metals was due to ultra-violet light alone.

The alkali metals, on the other hand, were very sensitive to light of wave-lengths within the range of the visible spectrum as well as to ultra-violet light. The leak of negative electricity from an illuminated plate occurred whether the metal was surrounded by a gas or was in the best vacuum obtainable, but the *rate* at which the leak took place varied considerably with the nature and pressure of the surrounding gas. Investigations were made by Stoletow and others soon after the discovery of the effect to determine the relations between the leak of electricity from the illuminated plate, and such factors as the pressure of the gas and the electric force outside the illuminated plate.

The emission of negative electricity from an illuminated plate is generally known as the photo-electric effect, or sometimes as the Hallwachs effect, Hallwachs being one of the first to investigate it. No satisfactory explanation, however, of the loss of negative charge by a metal when illuminated was given until the development of the theory of the ionisation of gases.

Gases in their ordinary state are almost perfect insulators. The simple electroscope shows this clearly. When the rod supporting the gold leaves is well insulated, the gold leaves will retain a charge for days, showing that the air, or other gas, in the electroscope has no appreciable conductivity. If now a flame, or an incandescent solid, be brought near the electroscope so that the hot gases have access to the gold leaves, or to some conductor in metallic connection with them, the leaves will immediately collapse, showing a complete loss of charge. The same thing happens if a beam of X-rays is directed into the electroscope, or if some radio-active substance is placed inside. Suitable control experiments show that the only possible explanation is that the gas, which in its normal state is an insulator, becomes conducting under the influence of these agents. From about 1896, very rapid progress was made by Sir J. J. Thomson and his pupils in elucidating the nature of the conductivity imparted to gases by various agents, and particularly by X-rays. The X-rays and other ionising agents are considered to produce a number of charged particles, or "ions," in the gas. These ions are molecules, or small aggregates of molecules, which differ from the rest in possessing electric charges, some negative and some positive. In an electric field they move towards the electrodes, their directions of motion depending on the signs of their charges. On arriving at the electrodes the ions give up their charges, and in this way the discharging effect of an ionised gas is explained.

The nature of ionisation was made still clearer by Sir J. J. Thomson's discovery of the existence of *electrons*, which are negatively charged particles whose masses are far smaller than those of atoms. The electron is now regarded as the ultimate unit of negative electricity. A positive charge, on the other hand, is not known to exist as a separate entity apart from atoms or molecules. The electrons when isolated by our experimental

methods are always moving with very high speeds, from  $10^7$  to  $10^{10}$  cm./sec. The fastest electrons may collide successively with a number of molecules, and the effect of each collision is to reduce the velocity of the electron. When the velocity has been reduced to about  $10^8$  cm./sec., the electron sticks to any neutral molecule or atom with which it collides and forms a negative ion. Since ionisation of a gas by X-rays is known to produce equal numbers of positive and negative ions, it is natural to explain the negative ion as a neutral molecule which has acquired an extra electron, and the positive ion as the neutral molecule from which the electron was originally emitted. The atom on the electron theory is regarded as an assemblage of electrons, probably in rapid motion, together with a positive nucleus, so that the atom as a whole is uncharged. The forces keeping the electrons in position are naturally assumed to be electrical. When sudden and violent changes occur in the atomic forces through the impact of a swiftly moving electron, or through the action of an X-ray pulse, or ultra-violet light, the atomic system may be so much disturbed that one of the electrons leaves the system altogether. In this way one pictures the phenomenon of ionisation. When ionisation is confined to the surface layers of a solid or liquid substance, only the electron can escape from the substance, while the positive charge, necessarily associated with the parent atom, remains in the surface. In the presence of a gas these electrons become negative ions. The electrons or negative ions, as the case may be, can be detected experimentally through the emission of negative electricity from the surface, provided the electric field is favourable. It is a characteristic feature of surface ionisation, however, that if the field is reversed there is no emission of positive electricity.

The experimental evidence, hitherto considered, indicates that the photo-electric effect is localized in the surface of the metal, that is to say, ionisation occurs in the surface itself—a phenomenon distinct from gaseous ionisation produced by X-rays. This view was firmly established by the experiments of Sir J. J. Thomson<sup>1</sup> and Lenard<sup>2</sup> who found that a metallic plate in vacuo,

<sup>1</sup> Sir J. J. Thomson, *Phil. Mag.* XLVIII. p. 547, 1899.

<sup>2</sup> Lenard, *Ann. d. Phys.* II. p. 359, 1900.

illuminated by ultra-violet light, emitted electrons.) These electrons have velocities of the order of  $10^7$  cm./sec., and thus are much slower than ordinary cathode or  $\beta$  rays. It is convenient to refer to the electrons emitted from illuminated metals as photo-electrons, thus indicating their mode of production, but it must not be taken as implying that they are in any way different from other electrons. This discovery of the emission of electrons from illuminated surfaces made it possible to formulate much more definite views about the whole subject of ionisation by light.) The primary action of the light is to ionise atoms in the surface, that is, to cause them to emit electrons, some of which get away from the surface and can be detected experimentally..

It may seem somewhat strange that ionisation by ultra-violet light manifests itself as a surface effect in solids and liquids, while ionisation by almost all other agents appears most evident in gases. Yet there is no fundamental distinction on this account. Ultra-violet light—provided extremely short wave-lengths are used—does ionise gases just as readily as X-rays. But with the ordinary sources of ultra-violet light, the surface effect is the only one observed, and the methods of investigating it differ considerably from the methods employed in studying gaseous ionisation.

With the progress of experimental knowledge, it has become clearer that each substance has a definite wave-length at which its photo-electric effect starts. Wave-lengths longer than this are incapable of causing the emission of photo-electrons, while all wave-lengths shorter than this are effective. The critical wave-lengths for the alkali metals are in the visible spectrum, for the other metals they are between  $\lambda 2500$  and  $\lambda 4000$ , and for the non-metals they lie beyond  $\lambda 2200$ , the wave-lengths being measured in Ångström units ( $10^{-8}$  cm.). The critical wave-length for oxygen is about  $\lambda 1350$ . There is considerable experimental difficulty in working with such short wave-lengths, and this has seriously hampered the study of ionisation of gases by ultra-violet light. In general, the more electro-positive an element is, the longer is the wave-length at which the ionisation begins. The critical wave-length at which the photo-electric effect starts has recently acquired an important significance, for on certain theories we can

immediately calculate from it the work that is necessary to take an electron away from its parent atom. This is a quantity of fundamental importance in the electrical theory of atomic structure, for it measures the potential energy between the electron in its equilibrium position and the rest of the atomic system. For this reason I have endeavoured to indicate, wherever possible, the wave-length at which the photo-electric effect starts for the substance investigated. Unfortunately there is often much uncertainty in arriving at a correct estimate, since many experimenters have approached the subject from quite a different point of view, and explicit information as to the effective spectral region is wanting. We may almost say that the critical wavelength at which the photo-electric effect starts completely characterizes the photo-electric behaviour of a substance so far as the fundamental process is concerned. Of course, the actual experimental photo-electric currents are influenced by a number of secondary effects such as the absorption of the active light and of the electrons by matter.

The photo-electric effect was among the first phenomena to receive an interpretation on the quantum theory of radiation. The characteristic feature of the quantum theory is that the transference of energy to or from the radiant form is not continuous, but takes place in small finite units. (An unexplained peculiarity of the theory is the necessary assumption of the variation of the unit of energy from one wave-length to another.) The unit of energy is directly proportional to the frequency of the radiant energy, and is therefore equal to  $hn$ , where  $n$  is the frequency and  $h$  a constant known as Planck's constant. Hence if the energy is completely transferred to the photo-electron when light ionises a molecule, the energy of the photo-electron should be proportional to the frequency of the light. Experiments have now shown quite definitely that this is the case. When the quantum theory was first applied to the photo-electric effect it was assumed that the light was molecular in structure, each "molecule" or unit containing an amount of energy  $hn$  which could not be subdivided, and therefore on interaction with matter was wholly transferred to the photo-electron. Although many experiments show a remarkable agreement with the predictions

of the quantum theory, it is such a radical departure from the classical views of the nature of radiant energy that many attempts have been made to explain the results on lines more in accordance with the older ideas. The view now prevalent is that the quantum theory gives the correct mathematical expression for the energy transformations, but gives no indication of the nature of the phenomena to which it is applied.

In discussing photo-electric experiments, it is often desirable to know what part of the spectrum produced the effect under consideration. As most investigators do not give any information on this point, beyond merely stating their source of light, it was thought that a short account of the various sources of light used in photo-electric experiments would be useful. This will be found in Chapter x, together with some observations on the regions of the spectrum of the light transmitted by a number of substances including quartz and fluorite.

## CHAPTER II

### IONISATION OF GASES AND VAPOURS BY ULTRA-VIOLET LIGHT

THE interpretation of experiments on gases is always much simpler than the interpretation of experiments on solids and liquids. This is due to the comparatively simple conception of the physical state of a gas which we have in the kinetic theory of gases. Not only is our picture of the molecular state of a solid or liquid much less defined and precise, but also the difficulty of interpreting our results is considerably increased by the necessity for taking intermolecular forces into account in any explanation which aims at completeness. A considerable amount of positive knowledge has been acquired as to the nature of ionisation by Röntgen rays, and much of this is due to the fact that the effect can be studied, with comparative ease, in gases. Thus we know indirectly from ionisation experiments, and more recently directly from C. T. R. Wilson's experiments, that ionisation by Röntgen rays consists, first of the expulsion of a number of corpuscles moving with high speeds from certain molecules, and secondly, of the ionisation of a much larger number of molecules by these corpuscles. But when we turn to ionisation by light, almost all the experiments have been concerned with the photo-electric effect at solid or liquid surfaces. The difficulties of interpreting such experiments with any degree of exactness has doubtless caused investigators from time to time to turn to the ionisation of gases by light. Unfortunately it has been extremely difficult to get any evidence of true ionisation of gases by light until comparatively recently, to say nothing of a detailed investigation of the phenomenon. The experimental difficulties are such that almost all the experiments are restricted to proving

that the ionisation exists, or does not exist, under certain conditions of illumination.

A general consideration of the photo-electric effect leads to the conclusion that the more electronegative an element, the more difficult it is to ionise it by light. In more precise terms, this means that the longest wave-length which is capable of ionising an element goes more and more into the ultra-violet as the element becomes more and more electronegative. All the gases and vapours which are convenient to use in ionisation experiments are electronegative, and it so happens that the wave-lengths which are effective in such gases can only be got experimentally with special precautions. For example, only specially selected specimens of clear fluorite will transmit the light which ionises air; all other solid substances are opaque to the light.

A few remarks on the peculiar difficulties met with in investigating ionisation by light should be useful at this point. As

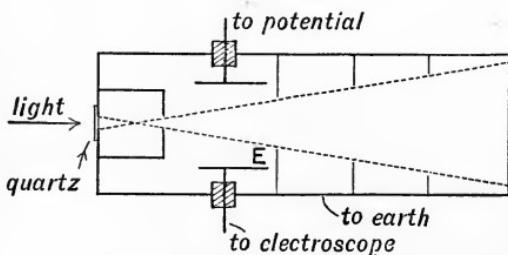


Fig. 1.

ionisation chambers usually have electrodes made of some metal or other conductor, spurious results are frequently obtained due to photo-electric action at the electrodes which give relatively big effects. The following is an example of spurious results of this kind obtained on one occasion and illustrates the care which must be taken in these experiments. An ionisation chamber of the form shown in Fig. 1 was made so that no light fell directly on the electrode  $E$ . The light passed in through a quartz window from a discharge in hydrogen. It is now known that this light is incapable of ionising air. Yet in this apparatus a small leak of the order  $10^{-15}$  amp. was always obtained. Now it was found that when the same light fell upon a surface of the same nature as the inside (lamp-black surfaces) of the ionisation vessel, a leak of

$10^{-10}$  amp. was obtained. The first leak of  $10^{-15}$  amp. might be accounted for by a trace of light finding its way to the electrode after several reflections. An amount only  $10^{-5}$  of the incident light would be sufficient, and it is difficult to be certain that this is not the true explanation of the leak. A decisive test was the following. A surface effect would decrease continuously as the pressure of the gas increased (assuming no ionisation by collision). A volume effect on the other hand would, at some stage or other, increase with the pressure. As the leak decreased with increasing pressure, it was concluded that the small effect obtained was merely a surface effect at the electrode.

Perhaps the best method of testing for ionisation by light is to illuminate a stream of gas and then to pass it through an ionisation chamber where the conductivity can be tested. If proper precautions are taken to prevent the entry of any light into the ionisation chamber, the presence of *positive* ions as well as negative ions in the stream of gas can be taken as conclusive evidence of the ionisation of the gas. Further tests must be made to determine whether the gas, or some impurity in it, is ionised, but at all events the effect is not due to a spurious surface effect. The presence of negative ions alone simply points to a photo-electric effect at the surfaces on which the light falls, in the neighbourhood of the window. The disadvantage of this method is that very large quantities of gas are required to sweep through the apparatus and the difficulties of ensuring a large supply of pure gas are considerable. This is the method which has been adopted by practically all investigators on ionisation of gases by light.

#### *Experimental Results for Air and similar Gases.*

The earliest experiments of any importance on ionisation of gases by light were those made by Lenard<sup>1</sup>. The light was obtained from an intense spark between metallic terminals. Air illuminated by this light was found to discharge both positively and negatively charged bodies, hence ions of both signs must have been present in the air. Most of the experiments were carried out with the unfiltered air of the room, though some experiments

<sup>1</sup> Lenard, *Ann. d. Phys.* I. p. 486, 1900; III. p. 298, 1900.

were made on dust-free gases. Ionisation of the same order was obtained in air, carbon dioxide and oxygen, a smaller effect in coal gas and a very small effect in hydrogen. The ionising light was found to be strongly absorbed by air, carbon dioxide and oxygen, and more strongly still by coal gas. In the case of the filtered gases, appreciable effects were only obtained when the spark was within a few mm. of the quartz window. / This indicates that the ionising light is located far in the ultra-violet. One peculiar result was that the ionisation was more powerful in fresh air than in air which had been illuminated for some time. Again, the mobilities of the ions produced in unfiltered air were measured and found to be  $3\cdot13$  cm./sec. for the negative ion and  $.0015$  cm./sec. for the positive ion—the latter being of quite a different order from the mobility of the positive ion produced by Röntgen rays, etc. These two observations point very strongly to the explanation that the conductivity observed is due to the presence of dust particles, or other nuclei, which emit electrons like ordinary surfaces when illuminated and remain positively charged. Their low mobility is explained by their great mass relative to that of the molecules and the fatigue-like effect is due to the removal of the positively charged particles by the electric field. Mobility experiments were not made with the filtered gases, hence it is not certain that the conductivity of the gases indicates that an ionisation of the gases themselves takes place, since ultra-violet light may produce in filtered gases nuclei which are photo-electric (p. 19).

Bloch<sup>1</sup> showed that the ionisation obtained by Lenard was really due to a photo-electric effect of the minute dust particles suspended in the air. On filtering the air, the number of positive ions produced was reduced to zero. It should be mentioned however that in a few experiments of Lenard the light had to traverse shorter distances than in Bloch's, and so Bloch's conclusions are not strictly applicable to these. However, when the light has to traverse 5 cm. of air or more and a quartz plate, Bloch's experiments show that filtered air is not ionised.

✗ The method of studying ionisation by means of condensation nuclei as developed by C. T. R. Wilson<sup>2</sup> is the most sensitive

<sup>1</sup> Bloch, *Le Radium*, p. 240, 1908.

<sup>2</sup> C. T. R. Wilson, *Phil. Trans. A. cxci.* p. 403, 1899.

method known for detecting small amounts of ionisation. When the air in the expansion apparatus was illuminated by Röntgen rays, large numbers of charged nuclei were produced. But while ultra-violet light also produced nuclei, they differed from the other nuclei in that they were *uncharged*. Wilson concludes that the nuclei produced by ultra-violet light are chemical products due to illumination of the air saturated with water vapour. When the ultra-violet light was very intense, clouds were formed with very small expansions or even without any expansion and lasted for a long time. Wilson points out that the drops cannot be pure water; he suggests that hydrogen peroxide is formed which, when dissolved in the water drops, alters the vapour pressure so that the drops remain in permanent equilibrium. Any real effect, which would be shown by the presence of charged nuclei, is masked in these experiments by the presence of vast numbers of uncharged nuclei which are produced photo-chemically. Wilson used a quartz window and the distance of the spark from it varied from a few cm. upwards. Hence the light probably did not contain wave-lengths shorter than  $\lambda 1770$ . It seems unfortunate that such an extraordinarily sensitive method for detecting ionisation should, in this particular case, be rendered useless by the production of photo-chemical nuclei which mask any real ionisation effect. Since these nuclei are produced by the interaction of water and oxygen, a way out of the difficulty would be to use some organic liquid, which did not give rise to photo-chemical nuclei, instead of water.

Sir J. J. Thomson<sup>1</sup> found that the light from a lime cathode discharge, after passing through a quartz window 3 mm. thick, produced a very small conductivity in a stream of gas passing the window. The natural conductivity in air was increased 8 times, in carbon dioxide 60 times, and in ammonia 150 times. The spectrum of the lime cathode discharge has probably never been investigated in the Schumann region (Chap. x), but we may take it that wave-lengths shorter than  $\lambda 1450$  are absent. From later experiments described below, it is concluded that pure air is not ionised by light of wave-lengths longer than  $\lambda 1350$ . With shorter wave-lengths very large ionisations were obtained. Possibly these

<sup>1</sup> Sir J. J. Thomson, *Proc. Camb. Phil. Soc.* xiv. p. 417, 1908.

experiments with the lime cathode discharge indicate that thin quartz transmits traces of light of the necessary short wave-lengths, but in far too attenuated an amount to be detected by the spectroscopic method. It is much more likely, however, that the very small effect obtained for air was due to the traces of impurities which, according to Lenard, are very difficult to get rid of, and which account for the conductivity in air when illuminated by the light passed through a quartz plate.

In 1910 the author<sup>1</sup> investigated the ionisation of air by ultra-violet light. The apparatus used is shown in Fig. 2. The source of light was a discharge in hydrogen at a pressure of about 1 mm. The filtered air streams up against the window *F* and then passes

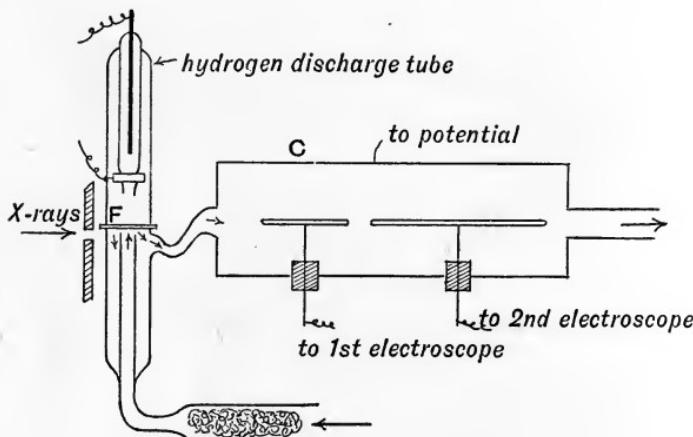


Fig. 2.

into the chamber *C* in which the conductivity is tested. Particular care was taken to prevent any light (except possibly after three reflections) from entering the testing chamber, which was of brass, and therefore photo-electrically active. The criterion for gaseous ionisation, as distinct from a mere surface effect, is the presence of positive as well as negative ions in the gas after illumination. When the window *F* was of quartz 3 mm. thick, no positive ions could be detected, though the apparatus was sensitive enough to detect a current of the order of  $10^{-15}$  amp. On substituting a certain plate of fluorite for the quartz, an enormous number of positive ions was obtained, the leak now being of the order of  $10^{-11}$  amp. The following control experiments

<sup>1</sup> Hughes, Proc. Camb. Phil. Soc. xv. p. 483, 1910.

were made. There was no leak (1) when the air was illuminated but at rest, and (2) when the air was in motion but not illuminated. The absence of nuclei which might emit photo-electrons as a surface effect when illuminated was confirmed by drawing the illuminated air from the testing chamber into a Wilson expansion apparatus. No drops or clouds were formed when the expansion was less than 1·25, showing the absence of nuclei larger than the ordinary ions.

It was desirable to find the wave-length of the light which produced the ionisation in air. From the experimental relations discussed in the next chapter we can find the shortest wave-length transmitted through a substance by measuring the maximum emission velocity of photo-electrons from a suitable surface illuminated by light passing through the substance. Several plates of quartz (3 mm. thick) gave practically identical emission velocities; hence their transparency limits are the same. According to Lyman, the transparency limit of such plates of quartz is  $\lambda 1450$ . On the other hand, the transparency limits of different pieces of clear fluorite were found to vary enormously. The only piece of fluorite which transmitted light capable of ionising air was unfortunately broken before its transparency limit could be ascertained. The most transparent of the other pieces of fluorite which did not transmit the ionising light was opaque to light of wave-lengths less than  $\lambda 1350$ . We may therefore conclude that air is not ionised appreciably by light of wave-lengths greater than  $\lambda 1350$ . It is unlikely that the best fluorite plate which was used transmitted light of shorter wave-lengths than Lyman's best specimens, and hence we may conclude from these experiments that the intense ionisation of air by ultra-violet light begins at some wave-length which is between  $\lambda 1250$  and  $\lambda 1350$ , and most probably nearer to the latter limit.

Some experiments were made on the mobilities of the positive ions produced in air by ultra-violet light, as Lenard's early experiments suggested that the positive ion produced by ultra-violet light was much heavier than that produced by other ionising agents. The apparatus shown in Fig. 2 was again used. Along the axis of the brass cylinder *C* there are two electrodes connected to tilted electroscopes. When the potential of the cylinder differs from

that of the electrodes, a radial electric field is established. In addition to having the same velocity as the gas parallel to the axis, the ions possess a radial velocity depending on the electric field and the mobilities of the ions. Hence, when the ionised air flows through the apparatus at a constant rate, the ratio of the charges received by the two electrodes is a function of the potential of the outer cylinder and the mobility of the ions. The ratio of the charge received by the second electrode to the total charge received by the two will give the proportion of the ions driven to the second electrode, and if we plot the

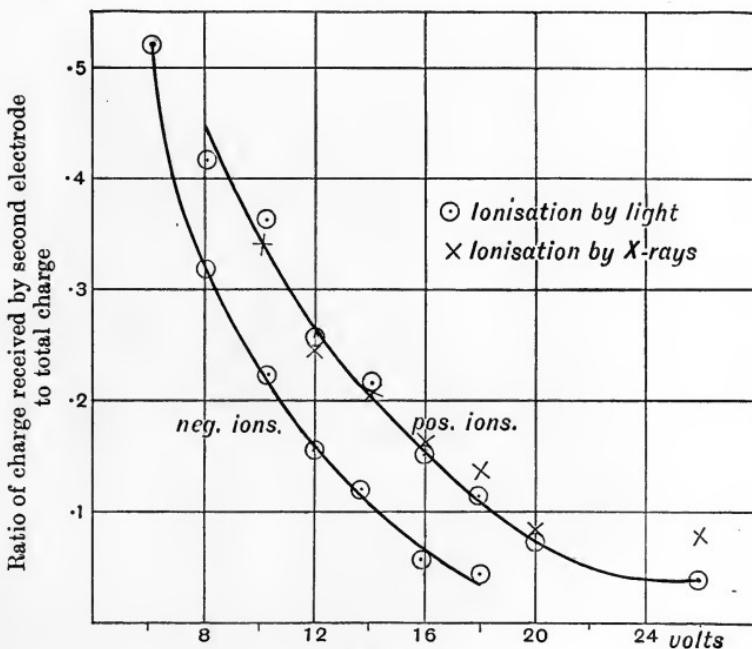


Fig. 3.

ratio of the charges against the potentials of the outer cylinder, when the stream of air is ionised alternately by Röntgen rays and ultra-violet light, the curves will coincide if the mobilities of the ions are identical. The ionisation by Röntgen rays was limited to a layer about .5 cm. thick just below the fluorite window, so that the distribution of the ions in the stream of air would be practically the same as when the air was ionised by ultra-violet light. Fig. 3 shows that the mobility of the positive ion is the same whether it is produced by Röntgen rays or by ultra-violet light. Hence so far as mobility is a criterion, the

positive ion produced by ultra-violet light is indistinguishable from that produced by Röntgen rays. Such a result naturally follows if we regard the positive ion as a molecule deprived of an electron by light in the one case and by the impact of a swiftly moving corpuscle in the other. There was no evidence of any positive ions possessing very small mobilities in these experiments.

Palmer<sup>1</sup> investigated the ionisation produced by ultra-violet light of short wave-length in a number of gases, viz. air, hydrogen, oxygen and nitrogen. The apparatus was identical in principle with that described above. A novel feature was the introduction of a small absorption cell 1 cm. long, bounded by fluorite windows, between the hydrogen discharge tube and the illuminated chamber through which the gas passed on its way to the testing apparatus. The absorption cell could be filled with oxygen at any desired pressure so as to alter the nature of the ionising light. Lyman's experiments showed that a fluorite cell containing oxygen transmits light belonging to the following spectral regions.

<i>Pressure of O<sub>2</sub></i>	<i>Region transmitted</i>
0	$\lambda$ 1250 to the visible spectrum
15 mm.	$\lambda$ 1250 to $\lambda$ 1350 and $\lambda$ 1500
40 mm.	$\lambda$ 1250 to $\lambda$ 1330 and $\lambda$ 1600
760 mm.	$\lambda$ 1250 to $\lambda$ 1270 and $\lambda$ 1760

In Fig. 4 the current is plotted against the pressure of oxygen in the absorption cell<sup>2</sup>. Equal numbers of positive and negative ions were obtained, the greatest leak being of the order  $10^{-11}$  amp. We see that the ionisation decreases rapidly as the range of wave-lengths transmitted in the neighbourhood of  $\lambda$  1300 becomes smaller. When there is no oxygen in the absorption cell, the number of ions produced in air is intermediate between that produced in oxygen and in nitrogen. When some of the light is cut out by the oxygen in the absorption cell, this no longer holds. Before we can interpret the results exactly, we should know whether the ionising light is completely absorbed in the stream of gas (1 cm. thick) and whether any recombination takes place on the way to the testing chamber. It is remarkable that the

<sup>1</sup> Palmer, *Phys. Rev.* xxxii. p. 1, 1911.

<sup>2</sup> I am indebted to Professor Palmer for the footnote to the curves which was omitted in the original paper through a printer's mistake.

ionisation in nitrogen should be so much greater than that in oxygen when we consider that oxygen absorbs light in this region of the spectrum much more strongly than nitrogen.

Palmer obtained a very small ionisation in hydrogen when the absorption cell was empty. Since the method of experiment requires large quantities of gas, it is difficult to be certain that the gas is absolutely pure and consequently some slight impurity may be responsible for the effect. Lyman found (spectroscopically) no trace of absorption of the Schumann region by hydrogen, and ionisation cannot take place without absorption. It must

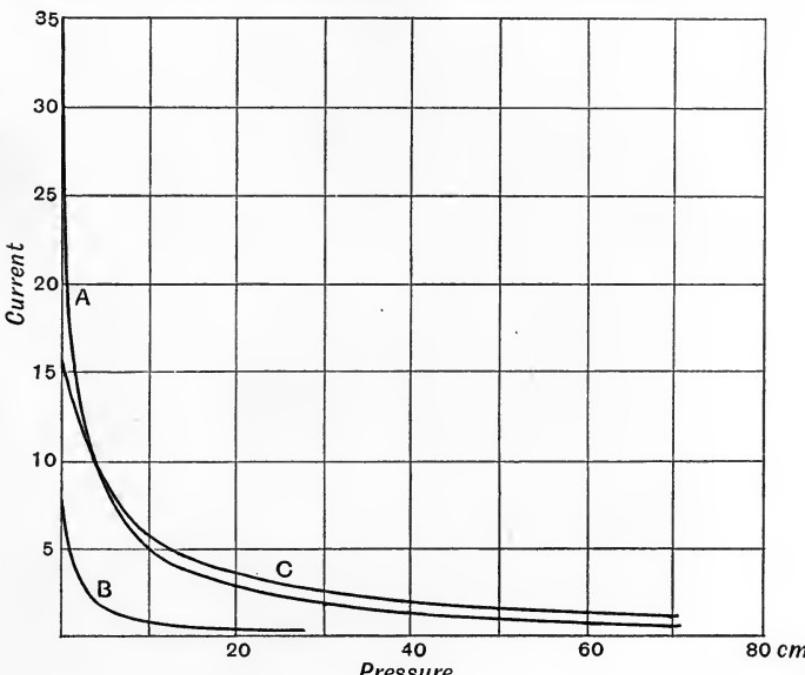


Fig. 4.

A, ionisation in nitrogen,  
B, " oxygen,  
C, " air.

be remembered, however, that ionisation tests are much more sensitive than absorption tests.

Palmer concludes that the ionisation of air by light begins with wave-lengths shorter than  $\lambda 1850$ . We think the evidence is in favour of displacing the limit much further into the ultra-violet. Even when the absorption cell was full of oxygen, some light of wave-lengths near  $\lambda 1250$  was transmitted and the ionisation might

be due to this. A decisive test for the existence of ionisation with wave-lengths greater than  $\lambda 1500$  could be made by using thin quartz instead of fluorite, but Palmer did not investigate this point.

Cannegieter<sup>1</sup> investigated whether the light due to an electrical discharge through a gas was specially effective in producing ionisation in the same gas, but concluded that such was not the case. The result that the ionisation is of the same order in hydrogen, nitrogen, carbon dioxide and air is quite opposed to all other researches on the subject and may possibly be accounted for by surface effects.

Lenard and Ramsauer<sup>2</sup> have made an elaborate series of experiments on the ionisation of gases by ultra-violet light and other problems arising therefrom. The source of light was a very intense spark between aluminium terminals, produced by a large induction coil which could take 90 amperes in the primary. The spark gap was in parallel with a condenser whose capacity was about .1 microfarad. With such a source of ultra-violet light, the intensity of ionisation in air was greater than has ever been obtained in cold gases except when cathode rays transmitted through a thin aluminium window were used. Part of the ionisation is attributed to a comparatively penetrating ultra-violet light whose wave-length is conjectured to be about  $\lambda 900$ . The authors investigated very thoroughly the rôle played by the suspended nuclei and gaseous impurities in the experiments on ionisation by light. The effect of such impurities is to mask, in an extraordinary manner, the real ionisation effects in air. Among the gaseous impurities which give misleading effects are carbon dioxide and ammonia. Both these are ionised by the quartz-violet. (Quartz-violet and fluorite-violet are convenient terms introduced by the authors and require no explanation.) Other impurities which give large effects are the vapours occluded on glass surfaces, in glass and cotton-wool and in rubber tubes. The compressed gases in cylinders contain some impurities which increase the ionisation due to ultra-violet light many times.

<sup>1</sup> Cannegieter, *Diss.*, Utrecht, 1911; *Ber. d. Akad. d. Wissenschaft. Amsterdam*, p. 1114, 1911.

<sup>2</sup> Lenard and Ramsauer, *Sitzungsberichte d. Heidelberger Akad. d. Wissen.* 1910—1911.

The authors found that it was necessary to purify the air by freezing out impurities in liquid air and to get rid of the occluded vapours by heating strongly all the glass tubing of their apparatus. It was only when this was done that spurious effects were avoided. Air purified in this way could only be ionised by the light which passed from the spark through a fluorite plate. When a quartz plate was substituted for the fluorite plate, the ionisation did not take place. The fluorite-violet produced an effect 5·7 times as great in carbon dioxide as in air. The quartz-violet produced an appreciable effect in carbon dioxide in addition. (Sir J. J. Thomson (*loc. cit.*) also found that carbon dioxide and ammonia were ionised by the quartz-violet.) The effect in hydrogen, purified by freezing out impurities by liquid air, was about equal to that in air. The hydrogen was from a cylinder and possibly contained air which may have accounted for the effect.

Traces of ammonia and carbon disulphide in air were found to increase the ionisation due to the fluorite-violet 44 and 14 times respectively. It may be mentioned here that similar results were obtained by Palmer<sup>1</sup> when the air contained traces of alcohol and ether. It is noteworthy that small quantities of water vapour in air did not produce any effect in the quartz-violet. In the fluorite-violet the presence of water vapour reduces the effect. The water vapour was found to produce considerable absorption in the light which ionised air. Hence when water vapour takes part in absorption as well as air, less ionisation is produced and one may conclude from these experiments that water vapour is less ionised (if at all) than air by the fluorite-violet.

Lenard and Ramsauer made experiments on the mobility of the ions and found that, under different conditions, ions varying much in size could be produced by ultra-violet light. Their conclusions may be summarized as follows. The ions are originally of molecular size, which indicates that they originate in much the same way as other ions. From experiments on the growth of the ions it was concluded that the very big ions were not produced by accumulation of molecules round a charged ion. The molecular ions do not grow to any extent in this way. The big ions are formed when solid or liquid particles (condensation

<sup>1</sup> Palmer, *Phys. Rev.* xxxii. p. 1, 1911.

nuclei) are suspended in the gas. The nuclei may be produced by the light itself. The small ions may collide with and stick to these big nuclei forming a heavy ion. There is no evidence that the heavy ions are built up by repeated additions to the charged nucleus. Condensation nuclei are produced in air by light unless it is carefully purified from condensable impurities by cooling. Solid nuclei of ammonium nitrate and nitrite appear to be formed when air containing traces of ammonia is illuminated by light of short wave-length. These nuclei can grow to a very large size. Hydrogen peroxide nuclei are also produced. Their size depends on the degree of saturation of water vapour present. So far as is known at present, chemical changes are not accompanied by ionisation.

Bloch<sup>1</sup> has verified the ionisation of air by Schumann rays. He also found that air could be ionised by the light from a mercury lamp. As the shortest wave-length available was probably  $\lambda$  1849, it seems likely that the effect observed was due to traces of impurities. It is not recorded whether he went to the same trouble as Lenard and Ramsauer did to remove these impurities. Bloch's arrangement enabled all the light emitted to be available for ionisation and hence the impurities had every chance to affect the results.

#### *Discussion of Results for Air.*

We shall now consider the experimental results given above and try to form some estimate of the longest wave-length which will ionise air. By air is meant the usual mixture of oxygen and nitrogen free from all other more condensable gases. One fact which is quite evident, is that in all the experiments in which abundant ionisation of pure air has been obtained, fluorite has been used instead of thin quartz. The hydrogen discharge used by Hughes and by Palmer is exceedingly rich in wave-lengths between  $\lambda$  1300 and  $\lambda$  1600 according to Lyman's investigations. Hence with thin quartz, very intense light with wave-lengths between  $\lambda$  1450 and  $\lambda$  1600 is available. No one has succeeded in showing that the light emitted by a hydrogen discharge and passed through quartz

<sup>1</sup> Bloch, *Comptes Rendus*, pp. 903, 1076, 1912.

produces any appreciable ionisation in air. In the experiments of the author, thin quartz and a piece of fluorite which only transmitted light of wave-length longer than  $\lambda 1350$  did not produce any measurable ionisation in air, while another piece of fluorite which could hardly have transmitted light of shorter wave-length than  $\lambda 1250$ , enabled an effect to be obtained  $10^3$  or  $10^4$  times as great as the least effect which could be detected. In Palmer's experiments, the fluorite absorption cell, filled with oxygen, always allowed some light in the neighbourhood of  $\lambda 1260$  to pass, so we cannot draw any certain conclusions from his work as to the problem in hand. It is significant that Lenard and Ramsauer did not obtain any ionisation in pure air with light which passed through quartz, though their source, being a very powerful one, was particularly well adapted to make any small effect evident. According to Lyman, the spectrum of the aluminium spark in air shows strong lines near  $\lambda 1300$ , weak lines near  $\lambda 1500$ , and strong lines near  $\lambda 1600$  and  $\lambda 1720$  to  $\lambda 1800$ . Thin quartz cuts out the  $\lambda 1300$  group. The  $\lambda 1500$  and  $\lambda 1600$  groups may possibly have been ineffective in Lenard and Ramsauer's work owing to absorption by air outside the window, as they do not explicitly state that they ever put the spark close up to the window when using quartz as they did when using fluorite.

From analogy with photo-electric experiments on metals, it seems likely that the ionisation of a gas sets in at some definite wave-length and increases with great rapidity with decreasing wave-length, and hence this critical wave-length should be fairly well defined. If we assume that the quantum theory is applicable to the problem in hand, we can calculate what the critical wave-length should be (p. 43). If  $V_0 e$  is the energy required to take an electron from a molecule, and if the electron is absorbing energy from light whose frequency is  $n$ , then the energy in the quantum,  $hn$ , must exceed  $V_0 e$  in order that ionisation should be possible. Taking  $h = 6.55 \times 10^{-27}$  erg sec.,  $e = 4.65 \times 10^{-10}$  E.S.U., and the critical wave-length to be  $\lambda 1350$ , we get for  $V_0$  the value 9.2 volts. Ionisation can be produced by the impact of an electron on a molecule. Before the electron can produce ionisation, its kinetic energy must exceed the energy required to ionise a molecule.  $Ve$  is the energy acquired by an electron moving freely between

two points whose potential difference is  $V$ . When  $V_e$  is equal to the energy required to ionise a molecule,  $V$  is called the ionising potential. The most accurate measurements of the ionising potentials are those of Franck and Hertz<sup>1</sup>, who give 9·0 volts for oxygen. (For nitrogen they give 7·5 volts and, working backwards, this indicates that ionisation in nitrogen should be possible with about a wave length of  $\lambda$  1620. However, before we get ionisation, we must have absorption and the absorption by nitrogen is scarcely observable until we get to shorter wave-lengths. A smaller ionising potential for nitrogen than for oxygen was hardly to be expected from indirect estimates based on ionisation by collision.) Our conclusion that  $\lambda$  1350 is the critical wave-length for oxygen is therefore in good agreement with theoretical deductions. A considerably larger value for the critical wave-length, such as  $\lambda$  1800, would be inconsistent with the indications of the quantum theory. In view of the wide application of the quantum theory to molecular physics and especially the simple explanation which it affords of the photo-electric effect, the experimental evidence does not seem strong enough to warrant our rejecting  $\lambda$  1350 as the critical wave-length for air in favour of a considerably longer wave-length.

### *Chlorine and Iodine.*

Ludlam<sup>2</sup> found that the fluorite-violet did not produce any ionisation in pure chlorine although marked effects were obtained with the same light in air. That the long wave-length limit should be shorter for chlorine than for air is to be expected, as it is one of the most strongly electronegative elements known.

The ionisation of iodine vapour has been sought by several investigators on account of the fluorescence which is produced in it by light of comparatively long wave-lengths.

Henry<sup>3</sup> and Whiddington<sup>4</sup>, both using the light from a carbon arc transmitted through quartz, could not find any ionisation. Franck and Westphal<sup>5</sup> confirmed these results, but most of the ultra-violet light was cut out by the glass of their apparatus.

<sup>1</sup> Franck and Hertz, *Verh. d. Deutsch. Phys. Ges.* xv. p. 34, 1913.

<sup>2</sup> Ludlam, *Phil. Mag.* xxiii. p. 757, 1912.

<sup>3</sup> Henry, *Proc. Camb. Phil. Soc.* ix. p. 319, 1898.

<sup>4</sup> Whiddington, *Proc. Camb. Phil. Soc.* xv. p. 189, 1910.

<sup>5</sup> Franck and Westphal, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 159, 1912.

They obtained the very interesting result that, while fluorescing iodine vapour was not ionised itself, it was easier to produce a glow discharge through the fluorescing iodine vapour than through the non-fluorescing vapour. Apparently, less work is required to separate an electron from a molecule when it fluoresces than when it does not.

It would have been interesting to investigate the ionisation in iodine vapour by the fluorite-violet. Being less electronegative than chlorine, ionisation might possibly be obtained.

### *Organic Vapours.*

Stark<sup>1</sup> investigated the conductivity of a number of organic vapours when illuminated by ultra-violet light. He obtained decisive evidence of ionisation in anthracene, diphenylmethane,  $\alpha$ -naphthylamine, and diphenylamine. The light used was that from a mercury lamp, which was not likely to emit wave-lengths shorter than  $\lambda 1849$ . The compounds were introduced into a highly exhausted quartz tube (about 3 cm. wide) provided with nickel-steel electrodes. The vapour pressure was varied by altering the temperature of the tube. At low temperatures, when the vapour pressure is quite negligible, the leak obtained on illumination must be due to the photo-electric effect at the electrodes. Provided ionisation by collision is avoided, this leak should decrease as the pressure of the vapour is increased, owing to absorption. But if ionisation occurs in the vapour itself, it will increase as the pressure increases until there is complete absorption of the ionising light. Beyond this, the leak should remain constant or decrease. In Fig. 5 the current through the illuminated tube is plotted against the pressure. The current due to the surface effect would be represented by some such curve as *a*, and that due to the ionisation of the vapour by *b*, while their sum represented by the curve *c* is that which is actually observed experimentally. One can only conclude definitely that there is ionisation in the vapour itself when the leak, at some stage or other, increases with the pressure. The following are the results obtained with anthracene and they are also typical of the results for the other substances. It will be observed that the ionisation current is quite a big one, in fact big enough to allow a galvanometer to be used.

<sup>1</sup> Stark, *Phys. Zeits.* x. p. 614, 1909.

The mercury lamp was placed close to the tube containing the anthracene.

	<i>Current due to illumination</i>
Lowest pressure (temp. $-70^{\circ}\text{ C.}$ )	$100 \times 10^{-10}$ amp.
As pressure increases, leak falls to	10      "
"      "      then rises to a max.	50      "
"      "      and finally decreases to	1      "

As the field never exceeded 4 volts per cm., the increase in the current with the pressure cannot be attributed to ionisation by collision. The pressure at which the maximum ionisation took place was estimated to be 40—50 mm. On measuring the leak corresponding to different voltages, it was found that the leak increased almost linearly up to 12 volts (the maximum tried).

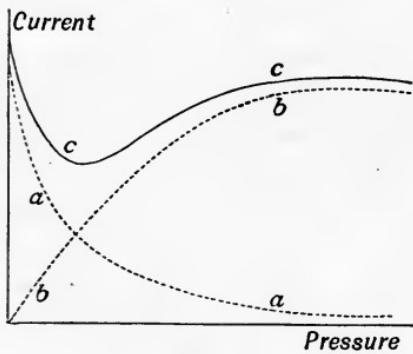


Fig. 5.

The current corresponding to this was  $1.2 \times 10^{-8}$  amp. and the 12 volts meant a field of about 5 volts per cm. Stark concluded from this that recombination was greater when the ionisation was produced by light than when it was produced by Röntgen rays, etc. The electrons have only a small velocity of separation and consequently they fall back into the parent molecule much more easily than if they had been electrons of high speed produced by Röntgen rays. In view of our later knowledge concerning ionisation by Röntgen rays, particularly from C. T. R. Wilson's experiments, Stark's explanation is by no means so attractive as it appeared at first sight. High speed corpuscles are produced by Röntgen rays, but their separation from their parent molecules is not the phenomenon of ionisation. Each high speed corpuscle in passing through the gas causes the ionisation of many molecules and this

process consists in the separation of electrons from molecules with velocities of the same order as those of photo-electrons. It seems probable that, with the same density of ionisation and the same fields, any other ionising agent would have given currents far from saturation. A test of this kind does not appear to have been made.

These vapours all show intense fluorescence when suitably illuminated. Stark developed a theory in which the fluorescence was identified with disturbances of the valency electron of the carbon atom of the condensed benzol ring. He considered that the ionisation and fluorescence were closely connected and therefore concluded that the same electron was involved in both effects.

Serkof, working in the Cavendish Laboratory, investigated the ionisation in a large number of organic vapours by Stark's method, improved in certain respects. The source of light was a mercury lamp. He obtained evidence of ionisation in only one vapour, viz. aniline, in addition to those which Stark found to be ionised. It is interesting to note that the aniline vapour had (compared with the other vapours) a large conductivity in the dark. It may be pointed out that the five vapours, in which Stark and Serkof obtained ionisation by the light from a mercury lamp, all contain the condensed benzol ring.

The writer<sup>1</sup> investigated the effect of ultra-violet light on a number of vapours. The vapours chosen were carbon disulphide ( $\text{CS}_2$ ), zinc ethyl ( $\text{Zn}(\text{C}_2\text{H}_5)_2$ ) and tin tetrachloride ( $\text{SnCl}_4$ ), each of which contains one element at least which has marked photo-electric properties. The light from a mercury lamp was used as the source and therefore the shortest wave-length available was  $\lambda 1849$ . Not a trace of ionisation was observed in any of the vapours, while they all absorbed the ultra-violet light powerfully. In the case of the zinc ethyl, the light which when totally absorbed in it did not produce any ionisation current greater than  $10^{-15}$  amp., produced a photo-electric leak from a zinc plate of the order  $10^6 \times 10^{-15}$  amp. It may be concluded therefore that light of wave-length longer than  $\lambda 1849$  is incapable of causing the emission of an electron from a molecule of these vapours. Analogous results were obtained when investigating the photo-electric effects of certain salts (Chap. VII). In the case of some salts however, it was observed that the light, while not producing a photo-electric effect, caused

<sup>1</sup> Hughes, *Proc. Camb. Phil. Soc.* xvi. p. 375, 1911.

a decomposition of the salt. A similar effect with these vapours was not looked for directly, but no striking evidence of such decomposition was noticed.

### *Metallic Vapours.*

Steubing<sup>1</sup> employed Stark's method to show that mercury vapour could be ionised by the light from a mercury lamp. The current obtained through the tube when the pressure of mercury vapour was zero was  $10^{-8}$  amp. This was the photo-electric effect at the electrodes. On increasing the vapour pressure of the mercury by heating, the current rose to a maximum value of  $6 \times 10^{-8}$  amp. The current was found to increase almost linearly with the potential difference up to 12 volts (the maximum employed) and it was suggested that Stark's explanation of the similar effect in the organic vapours applied also to the ionisation of mercury vapour by light. Steubing<sup>2</sup> points out that all the vapours in which he and Stark obtained ionisation have high molecular weights. ✓

The only other experiments on the ionisation of metallic vapours are those of Anderson<sup>3</sup> on potassium vapour. Experiments on the vapours of the alkali metals present many difficulties and the results are somewhat difficult to interpret. Anderson used visible light and caused his apparatus to go through a cycle of temperature changes. He found that the leak due to illumination, which increased with rise of temperature and therefore with the density of the vapour, did not diminish again with fall of temperature. This suggests that the effect observed was really due to a photo-electric effect at a thin imperceptible layer of potassium which was condensed on the electrodes, and not to a real ionisation of the vapour. It would be very useful for theoretical purposes to know whether the photo-electric effect sets in at the same wavelength for a substance in the gaseous state as in the solid state. It seems quite possible that the proximity and consequent interaction of the molecules, in the latter state, would enable an electron to be detached more easily from a molecule than when the molecule is isolated as in a gas.

<sup>1</sup> Steubing, *Phys. Zeits.* x. p. 787, 1909.

<sup>2</sup> Steubing, *Jahrbuch d. Radioaktivität*, April 1912.

<sup>3</sup> Anderson, *Phys. Rev.* (2) i. p. 233, 1913.

*Summary.*

Almost all the experiments on ionisation of gases by ultra-violet light have been concerned merely with establishing the existence of ionisation in gases and vapours under certain conditions. Our knowledge from such experiments of the nature and mechanism of ionisation by light does not extend beyond the fact that light produces ions in air of the same mobility as those produced by Röntgen rays. Up to the present, the experimental difficulties have prevented any detailed investigation of the way in which the ionisation depends upon the various factors in the problem. For example, it is almost impossible to study the ionisation of the permanent gases by monochromatic light as no apparatus is available which will isolate light of wave-lengths less than  $\lambda 1850$ . Longer wave-lengths may suffice for some vapours, but the necessity for maintaining these vapours at high temperatures introduces considerable experimental difficulties. The following are among the questions which remain unanswered. How does the number of ions produced in a gas by unit energy of light vary with the wave-length? Does this variation depend on the nature of the gas? How much of the energy of the ionising light appears as energy of ionisation? How does the ionisation depend on the temperature, pressure, and mixture of gases? Experiments on metallic vapours which may be ionised by light of sufficiently long wave-lengths are most likely to give the desired information. The answers to some of these questions are suggested, but only indefinitely, by investigations of the photo-electric effect of solids—metals in particular. There is always a good deal of uncertainty in the interpretation of experiments on solids. The number of electrons emitted by a solid surface when illuminated by light is a function of (1) the depth to which the light penetrates, (2) the velocity of the electrons released, since this determines the thickness of the layer from which the electrons can emerge, and (3) the physical state of the surface layers, including presence of occluded gases, incipient oxidation, etc. In so far as these effects cannot be taken into consideration quantitatively, the results of photo-electric experiments on solids are difficult to interpret with precision.

## CHAPTER III

### THE VELOCITIES OF EMISSION OF PHOTO-ELECTRONS

AN accurate knowledge of the velocities with which photo-electrons emerge from illuminated surfaces is of great importance in the discussion of the photo-electric effect. At the present time, the test afforded by our experimental knowledge of the velocities of photo-electrons is more conclusive and better adapted for discriminating between theories of ionisation by light than any other experimental evidence we possess in this branch of physics.

An illuminated plate emits photo-electrons with velocities ranging from a maximum velocity down to zero. We are chiefly concerned with the maximum emission velocity; the smaller velocities are probably due to loss of energy by the photo-electrons in passing molecules in the surface layers. The velocities of photo-electrons are almost invariably found from the potential difference which will bring them to rest. When an illuminated plate is at a positive potential with respect to the surrounding electrode, the electric force reduces the velocity of a photo-electron travelling away from the plate. If the potential difference is such that the gain of potential energy by an electron in moving from the plate to the surrounding electrode slightly exceeds its initial kinetic energy, the electron is brought to rest just before it reaches the surrounding electrode and then returns to the plate under the action of the electric force. Thus if we illuminate an insulated plate, initially at the same potential as the surrounding electrode, photo-electrons will leave it and its (positive) potential will increase until the kinetic energy of the fastest photo-electron is just insufficient to enable it to pass from the plate to the surrounding electrode. When this stage is reached, the potential of the plate does not increase any further. If  $V$  be the final potential difference,

then the potential energy gained by an electron in passing from the plate to the electrode is  $Ve$ . Since this must equal the initial kinetic energy of the fastest photo-electron, we have

where

$$e/m = 1.75 \times 10^7 \text{ E.M.U.}$$

This method of measuring the velocity of a photo-electron has led to the somewhat undesirable practice of referring to the velocity of an electron as a velocity of so many volts. The actual velocity in cm./sec. can always be found from the formula. Thus when an electron is said to have a "velocity of 1 volt," its real velocity is  $5.9 \times 10^7$  cm./sec. The actual velocity is proportional to the square root of the voltage.

The study of the emission velocities of photo-electrons resolves itself into an investigation of the relations between the velocities and (a) the intensity of the light, (b) its frequency and (c) the nature of the illuminated surface.

## *Effect of the Intensity of the Light on the Velocities of Emission.*

Lenard<sup>1</sup> first established the important result that the velocities of photo-electrons are independent of the intensity of the light producing them. This is of the greatest importance for it shows that the magnitude of the electric force in the beam of light does not determine the emission velocity. This result has since been verified by Ladenburg<sup>2</sup>, Millikan and Winchester<sup>3</sup>, Mohlin<sup>4</sup> and Elster and Geitel<sup>5</sup>. A very convincing verification of the fact is afforded by the recent experiments of Millikan in which the emission velocities of photo-electrons from a plate, illuminated by light of the same wavelength from a mercury arc and from an electric spark, were found to be identical. This was only established after the most rigorous precautions had been taken to exclude electric waves by completely enclosing the velocity measuring apparatus in a metal box. For some time it was thought that the spark produced photo-electrons

<sup>1</sup> Lenard, *Ann. d. Phys.*, viii, p. 149, 1902.

<sup>2</sup> Ladenburg, *Verh. d. Deutsch. Phys. Ges.* ix, p. 504, 1907.

<sup>3</sup> Millikan and Winchester. *Phil. Mag.* xiv. p. 188. 1907.

<sup>4</sup> Mohlin, *Akad. Abhandl.* Uppsala, 1907.

<sup>5</sup> Elster and Geitel, *Phys. Zeits.* ix, p. 451, 1908.

of higher velocity than the arc, but now these experiments must be regarded as still another striking illustration of the extreme difficulty of shielding off electric waves. Provided that adequate precautions are taken to shield the velocity measuring apparatus from electric waves, the velocities produced by the same wave-lengths from the arc and from the spark are identical (Millikan<sup>1</sup>, Pohl and Pringsheim<sup>2</sup>). Taking the mean intensity of the spark and arc to be of the same order, it is evident that the actual intensity of the spark during the short periods of illumination (separated by long periods of rest) is very much greater than that of the arc. Hence the identity of the velocities (for the same wave-length), when the plate is illuminated by the arc and spark in turn, proves that the emission velocities are quite independent of the intensity of the light.

The remarkably high values sometimes obtained for the velocities when electric sparks are used as sources of light arise in this way. The spark emits light and electric waves simultaneously. When the waves pass over the velocity measuring apparatus, the momentary potential difference between the illuminated plate and the surrounding electrode is by no means the steady potential difference given by the voltmeter. Hence the apparent potential difference as observed does not give us any idea of the effective potential difference at the instant of illumination and conclusions drawn from the apparent potentials are quite incorrect.

#### *Effect of the Frequency of the Light and the Nature of the illuminated Metal on the Velocities of Emission.*

The velocities of photo-electrons are known to depend on two factors, the frequency of the light used, and the nature of the illuminated metal. Early experiments showed that the shorter the wave-length of the light used for illuminating the metal, the greater were the velocities of emission of the electrons. In order to discriminate between theories of the photo-electric effect, it is necessary to know the mathematical form of the relation between the velocity and the frequency. Two laws have been put forward to represent the experimental results.

<sup>1</sup> Millikan, *Phys. Rev.* i. p. 73, 1913.

<sup>2</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xv. p. 974, 1912.

(1) According to one law, the maximum emission *velocity* of a photo-electron is a linear function of the frequency. Expressed in symbols, this is

$$\sqrt{V} = k'n - c,$$

where  $n$  is the frequency,  $k'$  and  $c$  are constants and  $V$  is the potential difference required to bring the fastest photo-electron to rest. By equation (1), p. 28,  $\sqrt{V}$  is proportional to its velocity. We shall refer to this law as the "velocity law." When simplified by the omission of the constant  $c$ , it is sometimes known as Ladenburg's law.

(2) The other law is that the maximum emission *energy* of a photo-electron is a linear function of the frequency, and is represented by

$V$  has the same meaning as before and is therefore proportional to the energy of the photo-electron.  $k$  and  $V_0$  are constants. We shall refer to this law as the '(energy law.)'

For a considerable period, the experimental results were not sufficiently accurate to decide between the two laws. The recent investigations of the author and of Richardson and Compton show, however, that the relation between the velocity and frequency is in good agreement with the energy law but not with the velocity law.

The relation between the velocity of the photo-electrons emitted from different metals and the frequency of the light is always found to be represented by equation (2), but the value of the constant  $V_0$  depends on the nature of the metal.

Equation (2) when put in the form

$$Ve = ke \cdot n - V_0 e,$$

in which the terms are of the dimensions of energy, suggests that  $ke \cdot n$  is, in some way or other, the amount of energy which the photo-electron has to begin with and that  $V_0 e$  may be looked upon as the sum of the energy lost in escaping from the parent atom and the energy lost in passing through the surface layer. If we assume that the latter does not exist when the metallic surfaces are prepared by distillation in vacuo, then  $V_0 e$  may be regarded in this case as the work spent in escaping from the atom.  $\times$

*Distribution of Energy among the Photo-Electrons.*

The current from the illuminated plate is often measured as a function of the potential difference between the plate and the surrounding electrode. The results are usually given in curves of which Fig. 6 is typical.

Accelerating potential denotes that the potential difference is in such a direction as to assist the escape of the photo-electrons. A retarding potential  $AO$  is just sufficient to stop all the electrons and therefore measures the maximum emission energy.  $Bb$  represents the number of electrons possessing velocities greater than that corresponding to  $Ob$  (volts). With accelerating potentials

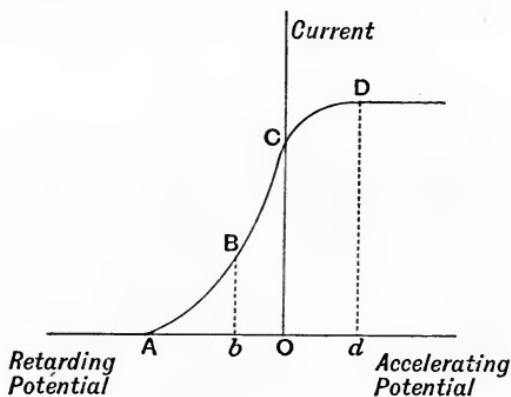


Fig. 6.

greater than  $Od$ , the photo-electric current is constant. It is evident that we can deduce from the curve the number of electrons possessing any given velocity. For this reason, such curves have frequently been termed "velocity distribution curves." This term is however not strictly correct, for the curves do not actually give a direct relation between the velocity and number. The part  $CD$  apparently indicates that a certain number emerge only when assisted by a small accelerating field. A variety of causes may contribute to this effect.

(1) Reflection of electrons. Some of the electrons leaving the illuminated plate may be reflected back again from the surrounding electrode. This return of electrons is prevented when the accelerating potential exceeds  $Od$ .

(2) Poor vacuum. If the electrons stick to molecules, then those molecules which happen to be travelling towards the illuminated electrode bring the charge back again. This effect is only prevented by an appreciable accelerating field.

(3) Stray magnetic fields of a few gausses. An electron of velocity corresponding to 1 volt would, in the absence of an electric field, describe a circle of radius 3·5 cm. in a field of 1 gauss applied at right angles to its direction of motion. If the apparatus is big enough to contain such an orbit, then an electron will get away from the illuminated plate to the surrounding electrode only when aided by a suitable accelerating field. Even when these three effects have been reduced to zero, the part *CD* may still be obtained.

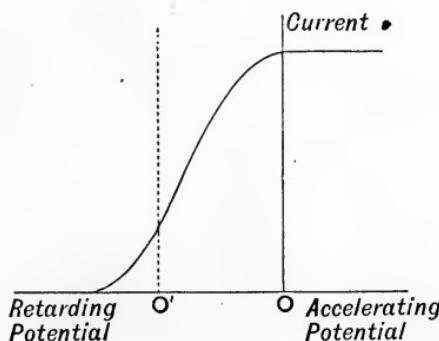


Fig. 7.

(4) A fourth source of this peculiarity in the curve has been discovered by Richardson and Compton<sup>1</sup>. The real potential difference between the illuminated plate and the surrounding electrode is that given by the measuring instrument *plus* (or *minus*) the contact difference of potential between them. Thus the *effective* field acting on the electrons involves the contact difference of potential. The curve, Fig. 7, relative to the broken ordinate as zero ordinate is what they obtained experimentally. (The disturbing effects already discussed were avoided in Richardson and Compton's experiments.) On allowing for the contact difference of potential, the zero ordinate has to be shifted by an amount *O**O'*. *The corrected ordinate always meets the curve where it begins to drop.* Hence all velocities from a maximum velocity down to zero are present and there are no electrons which emerge

<sup>1</sup> Richardson and Compton, *Phil. Mag.* xxiv. p. 577, 1912.

only with the help of an external field. Since the left-hand side of the experimental curve (Fig. 7) gives the relation between the energy (represented by the voltage) and the number of electrons possessing energies greater than that value, it is clear that the relative number of electrons emitted with any given energy is obtained by plotting the gradient of the curve in Fig. 7 against the retarding voltage. In this way the energy distribution curve (Fig. 8) is obtained from the experimental curve (Fig. 7). It is seen that the energies are distributed symmetrically about a mean energy.

Richardson and Compton's curves were obtained with monochromatic light. It is easily seen that even if photo-electrons emerge from their parent systems with identical velocities, outside the plate there will be a whole range of velocities from a maximum down to zero, owing to the electrons losing energy in passing from different depths in the plate before they escape at the surface. It is natural to regard the maximum emission velocity deduced from experimental observations as the real velocity of emission unaltered by collisions or other causes.

Even when all the effects previously discussed are avoided, the experimental curves may lead to incorrect views as to the distribution of energy among the electrons, unless the apparatus is of

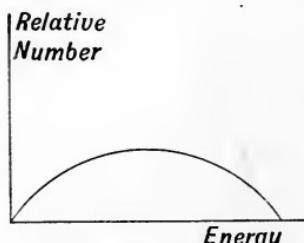


Fig. 8.

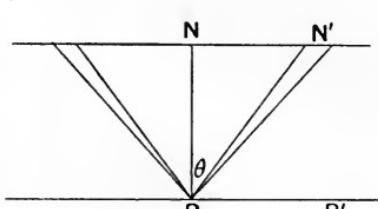


Fig. 9.

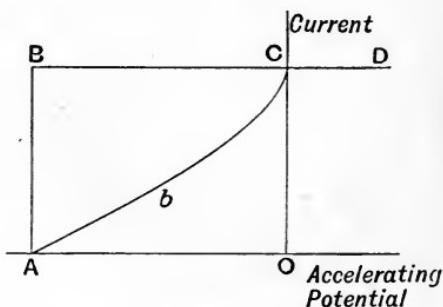


Fig. 10.

suitable form. An example will make this clear. Consider photo-electrons leaving the point  $P$  (Fig. 9) with equal velocities and in all directions. ( $PP'$  and  $NN'$  are two parallel planes.)

We shall see that the velocity distribution curve found by

experiment would not be *ABC* (Fig. 10) but *AbC*, which implies on the usual interpretation that all velocities from that corresponding to *AO* down to zero are present.

Let  $V_0$  be the potential required to stop an electron projected normally from the plate  $PP'$  by the time it reaches the plate  $NN'$ , which is at zero potential. The component of the velocity, perpendicular to the plate, of an electron which leaves the plate at an angle  $\theta$  with the normal is proportional to  $\cos \theta$  and the kinetic energy associated with this component is therefore proportional to  $\cos^2 \theta$ . Hence the potential required to turn the electron so that it just grazes the plate  $NN'$  is  $V_0 \cos^2 \theta$ . If this potential difference be applied, only those electrons which leave  $PP'$  at an angle with the normal less than  $\theta$  will reach the plane  $NN'$ . If  $n$  be the number of electrons leaving unit area of the plate  $PP'$  through unit solid angle, the number leaving the plate at an angle less than  $\theta$  will be proportional to

$$n \int_0^\theta \sin \theta d\theta \text{ or } n(1 - \cos \theta).$$

Thus a number of electrons proportional to  $1 - \cos \theta$  have a minimum apparent energy proportional to  $\cos^2 \theta$ . Therefore the relation between the number of electrons which appear to possess energies above a certain amount, and that amount, is parabolic. The experimental curve *AbCD* has no resemblance to the curve *ABCD* from which the true distribution of energies can be obtained.

Though this is an extreme case, it illustrates the caution one must observe in discussing so-called velocity distribution curves. Whenever an electron approaches a boundary with an appreciable tangential velocity, then the potential difference just necessary to stop it is less than the potential which corresponds to its actual velocity. In Richardson and Compton's arrangement, in which a small illuminated plate was surrounded by a large spherical electrode so that the field was radial, this effect was avoided and therefore the true distribution of energies could be obtained immediately from the experimental curve.

Van der Bijl<sup>1</sup> has shown lately how easily misleading energy distribution curves can be obtained and has confirmed Richardson and Compton's discovery of the influence of contact potential.

<sup>1</sup> Van der Bijl, *Verh. d. Deutsch. Phys. Ges.* xv. p. 330, 1913.

*Experimental Results.*

Ladenburg<sup>1</sup> was the first to investigate the relation between the maximum emission velocities of the photo-electrons and the wave-length of the light. The metals used were Pt, Zn and Cu. They were unavoidably exposed to the atmosphere between the time of polishing and the exhaustion of the apparatus. The potentials to which the plate rose when illuminated by different wave-lengths are given in the following table. The maximum emission energies are proportional to the potentials and the actual values can always be obtained by multiplying by  $e$ , the charge on an electron, as in equation (1), p. 28.

Ladenburg found that his results could be represented by the equation  $\sqrt{V} \cdot \lambda = \text{const.}$ , where  $V$  is proportional to the maximum energy. According to this, the maximum velocity of emission is proportional to the frequency, or the maximum energy is proportional to the square of the frequency.

TABLE 1.

Wave-length	Potentials measuring the maximum emission energies		
	Pt	Cu	Zn
$\lambda$ 2600	1.075 volts	1.01 volts	.685 volts
$\lambda$ 2420	1.28 "	1.16 "	.79 "
$\lambda$ 2290	1.49 "	1.33 "	.95 "
$\lambda$ 2180	1.60 "	1.46 "	1.00 "
$\lambda$ 2100	1.76 "	1.55 "	1.07 "
$\lambda$ 2010	1.86 "	1.69 "	1.12 "

Joffé<sup>2</sup> showed that Ladenburg's results would satisfy equally well the law that the energy (velocity squared) was a linear function of the frequency. The range of wave-lengths used by Ladenburg was too small to determine whether the results lie on a straight line or on a short piece of a parabola, a long way from the vertex.

It will be observed that the more electropositive the metal, the smaller the velocities. Ladenburg did not allow for the contact

<sup>1</sup> Ladenburg, *Verh. d. Deutsch. Phys. Ges.* ix. p. 504, 1907.

<sup>2</sup> Joffé, *Ann. d. Phys.* xxiv. p. 939, 1907.

potential difference which accounts in part, if not wholly, for the order of the velocities recorded.

Millikan and Winchester<sup>1</sup> investigated the emission velocities of photo-electrons from eleven metals. The metals were polished with dry emery, washed with alcohol and then dried. As in Ladenburg's experiments, they were in contact with the atmosphere for some time before the necessary vacuum could be obtained in the apparatus. The unresolved light from a spark was used and passed through air and a quartz plate. Hence the shortest available wave-length exceeded  $\lambda 1750$ . The order of velocities found was appreciably different from that given by Ladenburg. This must be attributed to slight differences in the treatment of the surfaces, which has an important influence in photo-electric experiments.

Attempts of various kinds were made by different experimenters to avoid complications arising from surface films. It was at one time thought that treating a surface as cathode in a discharge at low pressures, so that the exterior was removed by sputtering, would expose a new uncontaminated surface suitable for photo-electric experiments. Using such surfaces, von Baeyer and Gehrt<sup>2</sup> found that energies as high as 6 volts could be obtained, and moreover, that the energies were identical for Au, Al and Pt. This energy was considered to be the real energy of emission from the molecule. From similar experiments, the author<sup>3</sup> concluded that using the plate as cathode or anode merely resulted in an accelerating (sometimes a retarding) layer being formed on the plate. The charged ions travelling to and from the plate during the discharge may easily give rise to charged layers on the surface. That this explanation is the true one was verified later by von Baeyer and Tool<sup>4</sup>, who found that they could get the maximum emission energies to go up to 30 volts by more drastic treatment of the plate.

Klages<sup>5</sup> worked with a mercury surface which could be renewed in vacuo. Using the light from a mercury lamp, he obtained

<sup>1</sup> Millikan and Winchester, *Phil. Mag.* xiv. p. 188, 1907.

<sup>2</sup> von Baeyer and Gehrt<sup>s</sup>, *Verh. d. Deutsch. Phys. Ges.* xii. p. 870, 1910.

<sup>3</sup> Hughes, *Proc. Camb. Phil. Soc.* xvi. p. 167, 1911.

<sup>4</sup> von Baeyer and Tool, *Verh. d. Deutsch. Phys. Ges.* xiii. p. 569, 1911.

<sup>5</sup> Klages, *Ann. d. Phys.* xxxi. p. 343, 1910.

maximum emission energies corresponding to 2·3 volts. The shortest wave-length was probably  $\lambda 1849$ .

Kunz<sup>1</sup> concluded that his experiments on sodium-potassium alloy and on caesium were in better agreement with Ladenburg's law than with the energy law. Cornelius<sup>2</sup> investigated the effect for potassium and concluded that his experimental results were represented by a linear relation between the velocity and the frequency. The experimental arrangements in the experiments of Kunz and Cornelius do not seem to be satisfactory and no doubt affect the accuracy of their results. It should be mentioned that photo-electric experiments on the alkali metals are extremely difficult on account of the great susceptibility of these metals to contamination. For further discussion of these experiments, the reader is referred to Compton<sup>3</sup>.

Millikan and Wright<sup>4</sup> have published a number of researches in which they experimented on metals which were kept for a very long time in the highest vacua and which were illuminated for long periods by intense ultra-violet light. The result of this treatment was in general to increase the maximum emission energies from the normal 2 volts to about 15 or 20 volts. The explanation offered by Millikan and Winchester is that this treatment removes a surface film and that the electrons then emerge with their true velocities. More recent experimental investigations suggest that these high emission energies are due to accelerating films formed in some way on the surface. To test this, the contact potential difference should be measured during the course of the experiment. It is probable that the changes in the contact potential difference would run parallel with the change in the emission energies.

The inconsistencies of previous results led the author<sup>5</sup> to make a series of experiments on metallic surfaces prepared by distillation in vacuo. In this way the formation of the troublesome surface films was avoided. Much more consistent results were obtained than with ordinary polished surfaces. Careful measurements

<sup>1</sup> Kunz, *Phys. Rev.* xxix. p. 3, 1909; xxxi. p. 536, 1910.

<sup>2</sup> Cornelius, *Phys. Rev.* (2) i. p. 16, 1913.

<sup>3</sup> Compton, *Phys. Rev.* (2) i. p. 382, 1913.

<sup>4</sup> Millikan and Wright, *Phys. Rev.* xxx. p. 287, 1910; xxxiv. p. 68, 1912.

<sup>5</sup> Hughes, *Phil. Trans. A.* ccxii. p. 205, 1912.

were made to decide definitely, if possible, whether the maximum emission velocity, or the maximum emission energy, is proportional to the frequency. The apparatus used is shown in Fig. 11. The illuminated plate  $N$  was in metallic connection with

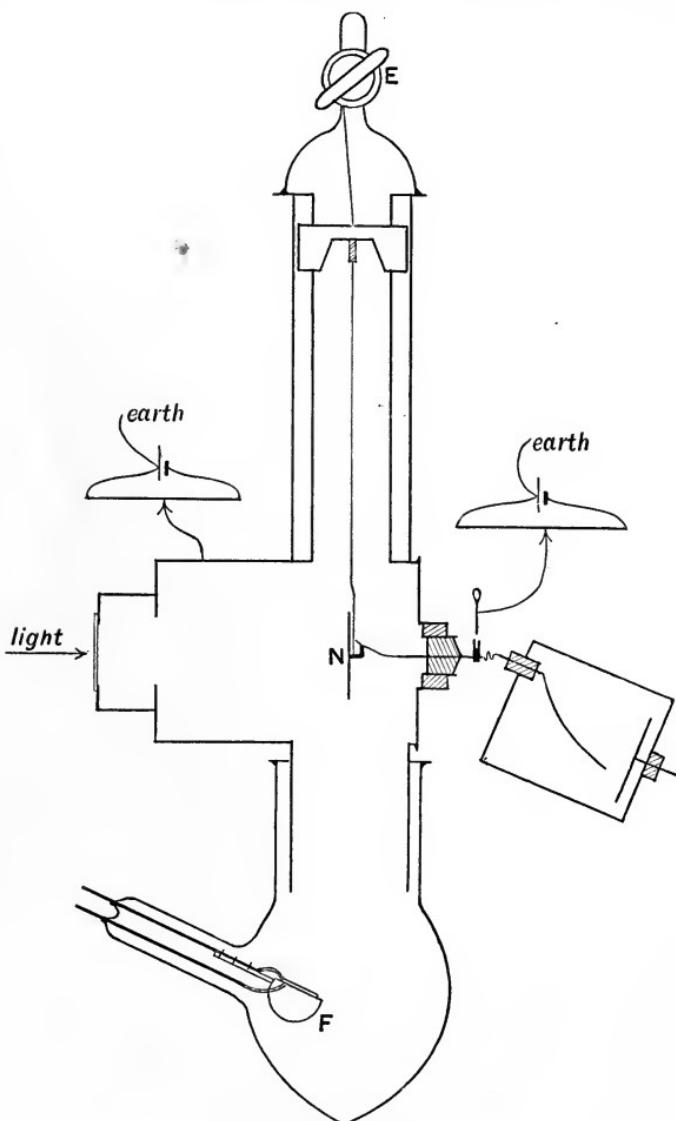


Fig. 11.

the tilted electroscope. Monochromatic light fell upon it, and the potential to which it rose under illumination was given by the electroscope. From this potential the maximum emission energy could be calculated. The metal to be distilled was contained in

the quartz furnace *F*. By means of the winch *E*, the plate *N* could be lowered until it was near *F* so that the volatilized metal condensed on it. From the time of formation to the time of illumination, the metallic surface was in the best vacuum obtainable by the liquid air method. The results for distilled cadmium are given in Table 2.

TABLE 2.

Wave-length	Experimental potentials measuring the maximum emission energies			Mean potentials
$\lambda 2537$	.901	.901	.890	.897 volts
$\lambda 2257$	1.420	1.431	1.431	1.427 "
$\lambda 1849$	2.480	2.480	2.480	2.480 "

Wave-length	Frequency <i>n</i>	Experimental potentials <i>V</i>	$V = kn - V_0$	$\sqrt{V} = k'n - c$
$\lambda 1849$	$1623 \times 10^{12}$	2.480 volts	[2.480]	[2.480]
$\lambda 2257$	1329 "	1.427 "	1.424	1.339
$\lambda 2537$	1182 "	.897 "	[.897]	[.897]
$\lambda 2967$	1010 "	.148 "	.286	.495
$\lambda 3126$	960 "	0 "	.101	.398
$\lambda 3340$	898 "	No effect	(-.12)	.293

$$\text{Constants in } V = kn - V_0, \quad V_0 = 3.347 \text{ volts}, \quad k = 3.590 \times 10^{-15}.$$

In the fourth and fifth columns we have the theoretical values for the potentials corresponding to the maximum energies calculated on the energy law and on the velocity law respectively. The two values in square brackets were used to determine the constants.

The proof of the linear relation between the maximum energy and the frequency depends mainly on careful observations recorded for  $\lambda 1849$ ,  $\lambda 2257$  and  $\lambda 2537$ . Comparing the third and fourth columns, we see that the experimental potential and the theoretical potential, calculated on the energy law, for  $\lambda 2257$  agree to .003 volt. On the other hand there is a difference of .083 volt between the experimental potential and that calculated on the velocity law. Additional confirmation is supplied by the fact that the photo-electric effect sets in between  $\lambda 3126$  and  $\lambda 3340$  which agrees with the energy law but not with the velocity law. (The velocities corresponding to  $\lambda 2967$  and  $\lambda 3126$  are

smaller than the predicted values on account of the earth's magnetic field being sufficient to cause the slow electrons to describe almost complete circles inside the apparatus.)

For each metal, several tables similar to that given above were obtained and in every case the energy law was verified.

The results are summarized in the following table. The linear relation,  $V = kn - V_0$ , connecting the energy and the frequency is completely characterized by the constants  $k$  and  $V_0$ . Hence the experimental velocities, corresponding to any wave-length, can be deduced readily. When  $V$  is plotted against  $n$ , the intersection of the line with the axis of abscissae determines the wave-length  $\lambda_0$  at which the effect sets in.

TABLE 3.

Element	Atomic weight	Atomic volume	Valency	$k$	$V_0$	$\lambda_0$
Ca	40·1	25·4	2	$3\cdot17 \times 10^{-15}$	2·57 volts	3700
Mg	24·3	14·0	2	3·39 "	3·08 "	3300
Cd	112·4	13·0	2	3·66 "	3·49 "	3140
Zn	65·4	9·2	2	3·79 "	3·77 "	3016
Pb	207·1	18·1	4	3·55 "	3·42 "	3115
Bi	208·0	21·2	5	3·63 "	3·37 "	3233
Sb	120·2	18·1	5	3·69 "	3·60 "	3075
As	75·0	13·1	5	$\Delta 3\cdot7$ "	$\Delta 4\cdot5$ "	2360
Se	79·2	17·6	6		$\Delta 4\cdot8$ "	$\Delta 2200$
O <sub>2</sub>	16·0	12·6	6		$\Delta 8\cdot0$ "	1350

*Note.* The constants  $V_0$  for Se and O<sub>2</sub> were obtained indirectly. As  $k$  does not vary much, a mean value  $3\cdot66 \times 10^{-15}$  was taken and the velocity for Se corresponding to  $\lambda$  1849 was determined. For O<sub>2</sub> the wave-length at which the ionisation sets in was assumed to be  $\lambda$  1350. Taking the mean value of  $k$  again we get  $V_0 = 8$  volts. For further observations on the ionising potential for O<sub>2</sub> see p. 20.

The values of  $k$  and  $V_0$  appear to change regularly with the atomic volumes for elements of the same valency, but there is a discontinuity (always in the same direction however) as we pass from one valency to another. The connection with the atomic volume is much more marked than with the atomic weight (cf. Ca, Mg, Zn, and Cd). The variations in  $k$  are much smaller than those in  $V_0$ , but they are somewhat bigger than the possible errors

of experiment. Moreover they change regularly with the atomic volume in the same way as  $V_0$ .

Richardson and Compton<sup>1</sup> carried out an important investigation on the emission velocities of photo-electrons. To obtain the real emission velocities, they allowed for the contact potential between the illuminated surface and the surrounding electrode. The maximum emission energy was a linear function of the frequency, thus independently confirming the conclusions arrived at by the author. For each wave-length, both the maximum emission energy and the mean energy of the photo-electrons were determined. Richardson and Compton consider the determination of the mean energies to be rather more accurate and prefer to employ them in deducing the characteristic  $\lambda_0$  for each metal. The gradient  $k$  of the line connecting the maximum energy and the frequency is about the same for Na, Al, Mg, Zn, Sn, and Pt. The authors consider the small variations in  $k$  to be accidental and within the errors of experiment, and so no relation between  $k$  and some other property of the atom was looked for. They obtained a considerably smaller gradient for Cu and Bi, for which no explanation is offered. Their results are summarized in the following table:

TABLE 4.

Metal	Values from maximum energies		Values from mean energies	
	$k$	$\lambda_0$	$k'$	$\lambda_0'$
Na	$3.3 \times 10^{-15}$	5830	$1.7 \times 10^{-15}$	5770
Al	2.8 "	4770	1.7 "	4110
Mg	3.3 "	3820	1.6 "	3750
Zn	3.2 "	3760	1.8 "	3570
Sn	3.1 "	3620	1.8 "	3370
Bi	2.3 "	3300	1.2 "	3370
Cu	2.4 "	3000	1.1 "	3090
Pt	3.75 "	2800	1.8 "	2910

The units of  $k$  are the same as those in Table 3.  $k'$  is very nearly  $\frac{1}{2}k$  on the whole, hence the energies are distributed equally about the mean energy, or the curve in Fig. 8 is symmetrical. The values of  $\lambda_0$  given by Richardson and Compton are somewhat greater than those given by the author in Table 3.

<sup>1</sup> Richardson and Compton, *Phil. Mag.* xxiv. p. 576, 1912.

An interesting point relating to contact potential arises out of a comparison of the two researches just discussed. The velocities of photo-electrons from say Zn, as usually determined, are less than the velocities from the more electronegative elements (e.g. Table 1). On allowing for the contact potential difference (as in Richardson and Compton's work) it is found that the order of the velocities is inverted. But the order of the velocities from distilled metals is in better agreement with the velocities corrected for contact potential than with the uncorrected velocities. This suggests that there should be little or no contact potential difference between metals distilled in *vacuo* and consequently that the ordinary contact potential arises directly from the differential effect of air (or other gases) on metallic surfaces.

### *Effect of Temperature on Emission Velocities of Photo-Electrons.*

Several investigators have made experiments to see whether the maximum velocities of emission of photo-electrons depend upon the temperature of the illuminated surface. Ladenburg<sup>1</sup> found that the velocities of the photo-electrons from Au, Pt and Ir were independent of the temperature up to 800° C. Kunz<sup>2</sup> found this to be the case for Na-K alloy (no temperature range given), Millikan and Winchester<sup>3</sup> for eleven metals from 15° to 125°, and Lienhop<sup>4</sup> for temperatures down to - 180°. It may therefore be concluded that the velocities of emission of photo-electrons are independent of the temperature of the illuminated surface over a wide range.

### *Theories of the Photo-Electric Effect.*

*Quantum theory.* From the two researches discussed above, it may be concluded that the linear relation between the maximum emission energy and the frequency has now been established definitely. There is still, however, some obscurity as to the interpretation of the gradient of the line,  $V = kn - V_0$ . The

<sup>1</sup> Ladenburg, *Verh. d. Deutsch. Phys. Ges.* ix. p. 165, 1907.

<sup>2</sup> Kunz, *Phys. Rev.* xxix. p. 174, 1909.

<sup>3</sup> Millikan and Winchester, *Phil. Mag.* xiv. p. 188, 1907.

<sup>4</sup> Lienhop, *Ann. d. Phys.* xxi. p. 281, 1906.

quantum theory of light was first applied to the photo-electric effect by Einstein<sup>1</sup>. If the energy in the quantum  $hn$  is wholly transferred to the photo-electron, then we have

$$Ve = hn,$$

and if by the time the electron emerges it has lost an amount of energy  $V_0e$ , then

$$V = (h/e)n - V_0.$$

This at once leads to the correct variation of  $V$  with  $n$ . The coefficient of  $n$  is  $h/e$  and is numerically equal to  $4.19 \times 10^{-15}$  if we take  $h = 6.55 \times 10^{-27}$ ,  $e = 4.65 \times 10^{-10}$  E.S.U. and  $V$  in volts. The actual values of the coefficient determined experimentally range from  $3.17$  to  $3.79 \times 10^{-15}$  (Table 3). Had the experimental values of  $k$  been grouped about the theoretical value  $h/e$ , it would have been natural to conclude that  $k$  is probably constant for all metals and equal to the quotient of these two universal constants. However the experimental values are well outside the theoretical value. There is no reason on the quantum theory why all the energy in the quantum  $hn$  should be acquired by the photo-electron; it may be shared between the electron and its parent molecule and the sharing may depend upon the nature of the molecule, thus giving rise to variations in  $k$ .

Yet the common occurrence of this constant  $h$  in so many branches of physics prevents us from dismissing finally the possibility that, though the experimental results are represented by  $V = kn - V_0$ , yet the more fundamental underlying process is represented by  $V = (h/e)n - V_0$ . Let us see how this could arise. The change from one to the other could be attributed to some process which reduces the energies of the photo-electrons in the same proportion. This would mean that the reduction in the energy would be proportional to the energy. It is difficult to imagine any such process. A surface layer would reduce all the energies by the same amount. The author (*loc. cit.*) found that the effect of admitting oxygen to a distilled surface of Cd was to shift the line  $V = kn - V_0$  parallel to itself. Again the mean  $k$  was about 16 % less than  $h/e$  and in Richardson and Compton's experiments about 20 % less. Yet, though there was a great

<sup>1</sup> Einstein, *Ann. d. Phys.* xvii. p. 132, 1905.

difference in the state of the surfaces in the two researches, this did not seem to affect the value of  $k$  to any great extent.

A way of reconciling the theoretical and experimental results may be based on the fact that the emission energies of the photo-electrons emitted from a thin film are greater when they are emitted in the same direction as that in which the light is travelling than when they are emitted in the opposite direction. Robinson<sup>1</sup> found that the maximum energy on the emergent side of a thin platinum film exceeded that on the incident side by about 12 %. Taking  $ke$  for Pt to be  $5.85 \times 10^{-27}$  from Richardson and Compton's experiments and increasing this by 12 %, we get  $6.55 \times 10^{-27}$ , which is in numerical agreement with Planck's constant. Possibly the photo-electrons are emitted from their parent systems in the same direction as that of the incident light, and those which emerge from the illuminated surface in the opposite direction lose energy when their direction of motion is changed. Thus we should expect the maximum velocities of photo-electrons emitted from sheets of metal in a direction opposite to that of the incident light to be less than the theoretical values. More work on thin films is necessary before this explanation can be regarded as established. This single observation of Robinson on platinum is very suggestive and similar investigations should be extended to other metals.

It is instructive to compare the value of  $V_0e$  deduced from photo-electric experiments with values of the work done by an electron in escaping from a hot metal. Richardson gives 5.34 volts as representing the work done (per unit charge) when an electron escapes from hot platinum. The results given in Table 4 indicate that  $V_0$  for platinum is 3.86 volts calculated from  $V = kn - V_0$ . Even if we use  $V = (h/e)n - V_0$  instead, and assume that the photo-electric effect starts at  $\lambda 2910$ ,  $V_0$  only increases to 4.32 volts. It is possible that  $V_0$  varies slowly with the temperature though there appears to be no evidence for this either in photo-electric or in thermionic experiments. Of course the assumption is here made that electrons of the same kind are released in both effects. The free electrons are concerned in the thermionic experiments, it is not so certain that they are involved in photo-electric experiments.

<sup>1</sup> Robinson, *Phil. Mag.* xxv. p. 115, 1913.

There is no need to suppose that the explanation of the photo-electric effect on the quantum theory necessarily means that light is molecular in structure, though at one period it was assumed that such was the case. Attempts have been recently made to account for the results of the quantum theory in ways which do not require the assumption of a molecular structure in radiant energy<sup>1</sup>.

### *Richardson's Statistical Theory.*

Richardson<sup>2</sup> offers a theory of photo-electric phenomena based on thermodynamical and statistical principles. Consider a cavity in a piece of matter. Inside the cavity there is an atmosphere of electrons, the concentration of the electrons being a function of the temperature. Richardson finds that

$$n = Ae^{\int \frac{w}{R\theta^2} d\theta}$$

is the relation between the concentration of electrons and the temperature, where

$n$  is the number of electrons per c.c. in the atmosphere,

$A$  a constant depending on the nature of the matter,

$R$  the gas constant for a single electron

(hence the kinetic energy of an electron is  $\frac{3}{2}R\theta$ )

and  $w$  the latent heat of evaporation of an electron in ergs.

The usual methods of the kinetic theory of gases show that the number of electrons returning to the matter from the atmosphere per sec. is  $N = \beta n \theta^{\frac{1}{2}}$ , where  $\beta$  is a number calculated on the kinetic theory. Thus

$$N = \beta n \theta^{\frac{1}{2}} = \beta A \theta^{\frac{1}{2}} e^{\int \frac{w}{R\theta^2} d\theta} = A_1 \theta^{\frac{1}{2}} e^{-\frac{w_0}{R\theta}} \dots\dots\dots (3),$$

on substituting

$$w = w_0 + \frac{3}{2}R\theta,$$

where  $w_0$  is the work done by the electron against the forces tending to retain it in the matter.

<sup>1</sup> In a recent paper (*Phil. Mag.* xxvi. p. 792, 1913) Sir J. J. Thomson describes a model of the atom which leads to a number of results indicated by the quantum theory without the necessity of assuming that a wave front of light is discontinuous in structure. Among the results accounted for by this model is the relation between the energy and frequency in the photo-electric effect.

<sup>2</sup> Richardson, *Phil. Mag.* xxiii. p. 594, 1912; xxiv. p. 574, 1912.

Having calculated the number of electrons which arrive at the surface, Richardson proceeds to calculate the number which leave it. Let the energy density of the complete aetherial radiation which is in equilibrium with the matter at temperature  $\theta$ , between the frequencies  $n$  and  $n + dn$ , be

$$E(n, \theta) dn,$$

where  $E(n, \theta)$  is some function of  $n$  and  $\theta$ . The rate of absorption is

$$\frac{c}{4} \epsilon E(n, \theta) dn,$$

where  $c$  is the velocity of light and  $\epsilon$  the emissivity. The assumption is now made that the emission or absorption of unit quantity of radiant energy of frequency  $n$  causes the liberation of  $F(n)$  electrons. The total number of electrons emitted in unit time by the complete radiation is

$$N = \frac{c}{4} \int_0^\infty \epsilon F(n) E(n, \theta) dn \dots \quad (4)$$

Equations (3) and (4) must be identical for all values of  $\theta$ . Richardson employed Wien's formula for the complete radiation

$$E(n, \theta) = \frac{8\pi}{c^3} hn^3 e^{-\frac{hn}{R\theta}}.$$

The equation to be solved is therefore

$$\int_0^\infty \epsilon F(n) hn^3 e^{-\frac{hn}{R\theta}} dn = A_2 \theta^2 e^{-\frac{w_0}{R\theta}},$$

all the constants being included in  $A_2$ . The equation is satisfied by

$$\epsilon F(n) = 0 \quad \text{when } 0 < hn < w_0 \quad )$$

$$\text{and } \epsilon F(n) = \frac{A_1 h}{R^2 n^2} \left(1 - \frac{w_0}{hn}\right) \text{ when } w_0 < hn < \infty \quad \dots \dots \dots (5)$$

Hence there is no photo-electric emission with frequencies less than  $w_0/h$ . No experimental evidence is available for testing the predicted relation between the number emitted and the frequency<sup>1</sup>.

If the mean kinetic energy of the electrons which are emitted

<sup>1</sup> See however a recent paper by Compton and Richardson (*Phil. Mag.* xxvi. p. 549, 1913).

by light of frequency  $n$  is  $T_n$ , then the total energy  $E$  emitted under the influence of the complete radiation is

$$E = \frac{c}{4} \int_0^\infty T_n \epsilon F(n) \cdot E(n, \theta) dn.$$

The  $N$  electrons streaming inwards from the atmosphere bring with them  $2NR\theta$  units of energy per sec. Hence, substituting for  $N$ , we must have

$$\int_0^\infty T_n \epsilon F(n) hn^3 e^{-\frac{hn}{R\theta}} dn = 2A_2 R\theta^3 e^{-\frac{hn}{R\theta}}.$$

Provided that  $\epsilon F(n)$  is expressed as in (5), the solution is

$$T_n = hn - w_0 \text{ when } w_0 < hn < \infty.$$

This gives a linear relation between the maximum emission energy and the frequency as found by experiment. As a rule electrons lose energy by collisions in emerging and hence the presence of large numbers with velocities less than the maximum. Richardson points out that this theory does not involve the assumption that radiant energy is molecular in structure except in so far as it is implied in Wien's formula.

The statistical method gives no insight into the processes at work in ionisation by light. It is concerned only with deductions which can be made from the consideration of energy interchanges on a large scale, and not with those associated with individual molecules and electrons. Moreover the theory is developed under the assumption that the substance is in thermal equilibrium with complete radiation travelling with equal intensities in all directions. The experimental results are obtained with directed monochromatic light.

### *The Photo-Electric Effect as a Resonance Phenomenon.*

The explanation of the photo-electric effect on Einstein's quantum theory and on Richardson's statistical theory, while leading to results in good agreement with experiment, gives us no indication of the actual process which occurs. A theory, which makes some attempt to represent, more or less, the actual mechanism of the photo-electric effect, is in many ways more satisfactory to physicists than those theories which by their

nature are only concerned with energy interchanges and not with the individual molecules and electrons. All theories which deal with the actual mechanism of the photo-electric effect are based on some kind of resonance process. The undoubtedly complexity of atomic systems does not permit an accurate picture of the resonant system to be formed. The various resonant systems which are designed to meet the experimental results probably do not occur in their simple isolated forms in nature. Nevertheless these hypothetical systems are of considerable value and help in indicating the principal features of the actual systems responsible for the photo-electric effect.

As Lenard<sup>1</sup> pointed out, a simple linear system is inadequate to account for the facts. Imagine an electron capable of vibrating along a line being attracted towards a centre by a force varying directly as the distance. This system will respond to a train of waves of the same frequency passing over it. If we suppose that the electron breaks away when the amplitude exceeds a certain critical value, then it is evident that the emission energy will depend upon the energy acquired during the last half-period. This obviously depends on the light intensity and is therefore in contradiction with experiment. Lenard suggests that the process is most probably one in which the light in some way releases an electron whose energy is determined by the energy it had in its orbit and not to any appreciable extent by the energy in the light beam. In other words, the light acts as a kind of trigger, precipitating a state of instability in certain atomic systems resulting in the ejection of an electron.

One way of avoiding the objection made to the linear system is to consider an electron describing circular harmonic motion. Let us assume that at a distance  $R$  from the centre, the force stops, and that an electron which describes increasing circles will shoot out tangentially when it gets to this limiting distance. We have the ordinary equation for circular harmonic motion

$$mr\omega^2 = Fer,$$

whence

$$2\pi n = \omega = \sqrt{\frac{Fe}{m}},$$

<sup>1</sup> Lenard, *Ann. d. Phys.* viii. p. 149, 1902.

where  $n$  is the frequency,

$\omega$  the angular velocity,

and  $F$  the force on unit charge at unit distance.

To satisfy the experimental result we must have

$$\frac{1}{2}mR^2\omega^2 = \text{const.} \times n,$$

or 
$$\frac{F \times R^2}{n} = \text{const.}$$

Assuming  $F$  to be a constant, we see that the critical radius, or the distance of the boundary, must vary as  $n^{\frac{1}{2}}$ , or assuming the critical radius to be the same for all systems, the intensity  $F$  of force at unit distance must increase as  $n$ . No reason can be given for regarding either condition as likely to occur actually. (Strictly speaking, the amplitude of the electron in the system we are now considering would only increase in the manner implied above with circularly polarised light.) A formidable objection to this system is the following. Experiment shows that there must be systems capable of responding to all frequencies greater than a certain frequency. It is difficult to imagine any atom containing the large number of systems necessary for the purpose. Possibly, the charges in the atom are continually rearranging themselves and so  $F$  may fluctuate over a wide range of values. Thus a small proportion of atomic systems may at any given instant be isochronous with light passing over them. Since ionised molecules are exceedingly few compared with unionised molecules, it suggests that those which are ionised must have been at the moment of ionisation in a very special condition, for if we assume the wave front continuous, the state of the particular molecules can be the only thing which determines whether ionisation is to happen or not.

A field of force varying as some inverse power of the distance gives the condition that orbits of all periods are possible according to the distance from the centre. To satisfy the experimental results we must have

$$\frac{1}{2}mv^2 \text{ or } \frac{1}{2}mr^2\omega^2 = \text{const.} \times \omega,$$

also the law of force 
$$mr\omega^2 = \frac{Fe}{r^n}.$$

Hence  $n = 3$ . We must, however, take into account the loss of

kinetic energy of the electron in passing outwards through the field of force. The inverse cube leads to the result that the electron will have lost all its energy when far away from the centre of force. The system is therefore unsatisfactory. No other system in which the law of force is an inverse power will give us the kinetic energy at a great distance from the centre proportional to the frequency of the original orbit. Again no system in which the force changes continuously and symmetrically from the centre outwards (except when it is proportional to the distance) can exhibit resonance when the period of the applied force coincides with its natural period. The effect of a wave of suitable frequency in passing over a system of this kind is to cause the electron to pass into a new orbit whose period is different, and therefore resonance ceases. On similar lines, Herrmann<sup>1</sup> has criticized atomic models described by Lindemann and others. It seems clear therefore that no symmetrical field of force varying as some power of the distance from the centre can give results in agreement with experiment. The field in an atom is probably due to several charges localized in some definite order and consequently it is highly likely to be much more complex than the fields we have been considering.

Sir J. J. Thomson<sup>2</sup> has shown that the orbit of an electron rotating on a certain cone (whose semi-vertical angle is  $\tan^{-1} 2$ ), at whose apex there is an electric doublet, is such that the energy is proportional to the frequency. If a light wave of the same frequency passes over the system, the system is disturbed and the electron goes off with much the same velocity as it had in its orbit. We must suppose that, at any given time, only very few atoms contain systems capable of responding to light of any particular wave-length. Such systems are not permanent; they are probably in a state of continual change, dissolving and forming again with different periods. Thus in a very large assemblage of molecules there will always be a number in a suitable state for ionisation by light.

It is evident from our discussion that simple resonance systems such as those based on harmonic motion are not adequate to

<sup>1</sup> Herrmann, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 936, 1912.

<sup>2</sup> Sir J. J. Thomson, *Phil. Mag.* xx. p. 238, 1910.

account for the results. We shall see later that, if we regard the wave front as continuous, an electron vibrating harmonically about a centre of force cannot absorb sufficient energy from the light waves to account for its energy of emission. It is therefore necessary to devise a system in which the energy of the photo-electron is not obtained from that of the light. Such a system would be one in which light of suitable frequency produced a state of instability resulting in the ejection of an electron with an amount of energy depending on the nature of the system and not on the intensity of the light. Sir J. J. Thomson's model is of this type and moreover gives the correct relation between the energy of emission and the frequency.

### *The Ionising Potential and Atomic Volume.*

Experimentally we find that there is a definite maximum wave-length, characteristic of each substance, at which the photo-electric effect starts. This has been interpreted as indicating the work necessary to take an electron away from the molecule of the particular substance. Table 3 shows that the work required for ionisation increases as the atomic volume decreases. One can see in a general way how this may arise. We may consider the atom as a positive charge localized at the centre of a sphere with the electron, having an equal negative charge, on the surface. (The positive charge is the algebraic sum of the positive nucleus and the other electrons which are situated near the centre.) The potential energy of the electron on the surface is  $e^2/r$ , where  $r$  is the atomic radius. The potential energy therefore varies inversely as the radius of the atom, or inversely as the cube root of the atomic volume. If we regard this electron as the photo-electron, then a consideration of the results for the metals given in Table 3 indicates that this relation is roughly correct if we keep to metals of the same valency. For two elements of the same atomic volume, but different valencies, the potential energy is greater in the case of that of the greater valency. This result

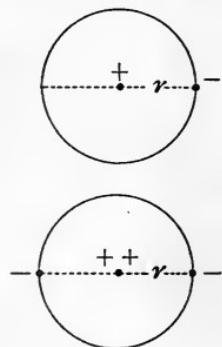


Fig. 12.

may be accounted for as follows. Let *A* represent a monovalent, and *B* a divalent atom. In the divalent atom we picture two electrons on the surface at opposite ends of a diameter, balanced by a double positive charge at the centre. The potential energy of one of the electrons in *B* is

$$\frac{2e^2}{r} - \frac{e^2}{2r} = \frac{3}{2} \frac{e^2}{r},$$

that is to say, it is greater than  $e^2/r$  for the monovalent atom. Similarly the potential energy between an electron and the trivalent atom of which it is a part would be greater than the energy in the case of a divalent atom and so on.

This point of view suggests that if we plot the ionising potentials  $V_0$  against the atomic volumes, and join all the points corresponding to elements of the same column of the periodic series, we should get a series of sloping lines one above the other. This is the case when we plot the results given in Table 3. So little is definitely known about the ionising potentials of the other elements, or, what for our purpose is the same thing, the critical frequency at which the photo-electric effect begins, that it is impossible to test this view as fully as one might desire. Certain experiments enable us to form rough estimates of the critical wave-length for a few non-metallic elements. The values for the critical wave-lengths lend some support to the view advanced above. An accurate knowledge of the critical wave-lengths for the different elements is much to be desired.

## CHAPTER IV

### THE TOTAL PHOTO-ELECTRIC EFFECT

#### *Influence of Gases on the Photo-Electric Current*

THE current obtained when light falls on a plate whose potential relative to the surrounding electrode is favourable to the escape of negative electricity, has frequently been regarded as a measure of the photo-electric effect of the plate. The results of such experiments, especially the earlier ones, are very conflicting. Later work has shown that the magnitude of the photo-electric current is affected to a great extent by a number of factors which, at first sight, do not seem to be directly connected with the photo-electric action.

The total photo-electric effect may be defined as the current emitted from an illuminated surface when its potential is favourable to the escape of negative electricity. This chapter gives an account of the relations between the photo-electric current and the factors on which it depends.

The photo-electric current, measured in the presence of a gas, is related to the number of photo-electrons set free per second at the illuminated surface in a very complicated manner. The gas has a two-fold effect. (1) The number of negative ions detected is a function of the nature of the gas and its pressure, and the potential difference between the electrodes, when the intensity of the light, and the number of photo-electrons released, remains constant. Under certain conditions of potential, ionisation by collision either in the body of the gas, or in the layer of gas adjoining the surface of the plate, comes into play. Another effect, that due to the inertia of the negative ions formed near the

illuminated surface, has also to be considered. (2) The gas may actually reduce the number of photo-electrons emitted from a plate by producing slight changes in the surface through occlusion or chemical action. This phenomenon will be treated in the section on photo-electric fatigue. For purposes of discussing effect (1), we assume that effect (2) does not come into play.

Fig. 13 gives the relation between the photo-electric current and the potential difference between the electrodes for different pressures<sup>1</sup>. The current corresponding to the pressure '008 mm.

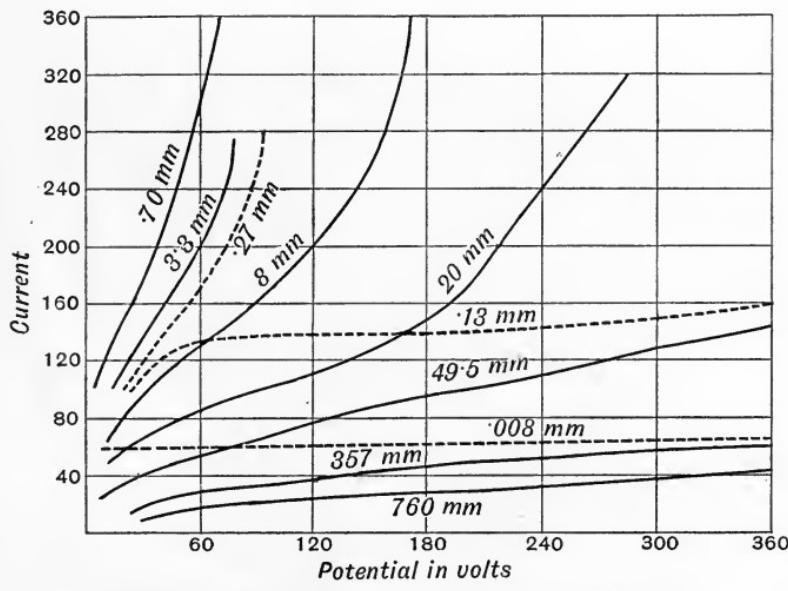


Fig. 13.

is independent of the potential difference and represents the number of photo-electrons released. The molecules of gas are too few to modify the amount of electricity escaping from the illuminated plate. The other curves however show the great influence of the gas on the photo-electric current. There is no approach to saturation when the gas is at a pressure of 760 mm. and the fields are much smaller than those necessary to produce ionisation by collision. The photo-electrons emitted from the plate probably

<sup>1</sup> Varley, *Phil. Trans. A.* ccii. p. 439, 1904.

stick to the first neutral molecules they hit, and consequently they all become negative ions very close to the surface of the plate. Now many of these molecules are travelling towards the plate and continue to do so after becoming negative ions. Thus a portion of the negative electricity is returned to the plate and the photo-electric current is less than the number of photo-electrons emitted. This effect persists even when considerable fields are applied, on account of the inertia of those ions travelling towards the plate and the small distance they have to go. To produce saturation, very strong fields would be required; but before this stage is reached ionisation by collision may set in. For the mathematical theory of the action described above, Sir J. J. Thomson's *Conduction of Electricity through Gases*, p. 268 (2nd edition), may be consulted.

When the field is strong enough, ionisation by collision throughout the volume of the gas will take place, thus magnifying the current passing between the two electrodes. Since the electrons are emitted with a finite velocity, a somewhat smaller electric field is required to produce ionisation by collision in a very thin layer of gas adjoining the illuminated electrode than in the body of the gas.

Stoletow<sup>1</sup>, v. Schweidler<sup>2</sup> and Lenard<sup>3</sup> have investigated ionisation by collision when an illuminated plate acts as a source of electrons. Consider two parallel plates, one of them illuminated and at a negative potential with respect to the other. On keeping the field constant, it is found that, as the pressure increases from zero, the photo-electric current increases to a maximum and then diminishes. Stoletow found that if the potential and the distance between the plates be  $v$  and  $l$  respectively, then the pressure  $p_m$  at which the current is a maximum is given by  $lp_m/v = \text{const.}$  Expressed in terms of the electric force and the mean free path of a molecule this becomes  $X\lambda = \text{const.}$  Unless the potential difference between the plates exceeds the ionising potential, ionisation by collision cannot take place.

<sup>1</sup> Stoletow, *Jour. d. Phys.* II. (9), p. 468, 1890.

<sup>2</sup> v. Schweidler, *Wien. Ber.* cviii. p. 273, 1899.

<sup>3</sup> Lenard, *Ann. d. Phys.* viii. p. 149, 1902.

The theory of ionisation by collision as applied to the photo-electric effect has been given by Sir J. J. Thomson (*Conduction of Electricity through Gases*, p. 271) and by Townsend (*Ionisation by Collision*, pp. 5, 30). As the calculations are not primarily concerned with the photo-electric effect, but with a different process merely initiated by photo-electrons, only a brief outline of the theory will be given.

Let  $n_0$  be the number of electrons which leave the illuminated plate and  $n$  the number of ions which arrive at the opposite plate at a distance  $l$ . If  $\alpha$  be the number of negative ions made by collision per cm., we have

where  $e$  is the base of the natural system of logarithms.

If  $\frac{X}{p}$  be kept constant, the potential drop along the free path is unaltered; hence the number of ions produced per collision is unaltered too. ( $X$  is the electric force between the plates,  $p$  the pressure.) The number of collisions  $\alpha$  per cm. which result in the formation of another ion is therefore proportional to  $p$  and hence we have

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right).$$

The form of the function  $f(X/p)$  has been determined by Townsend and is

$$\frac{\alpha}{p} = Ne^{-\frac{NVp}{X}} \dots \dots \dots (2),$$

where  $N$  is the number of collisions made by an ion in passing through 1 cm. of the gas at 1 mm. pressure, and  $V$  the potential fall along the free path which is necessary before an ion can be formed by collision. Substituting for  $\alpha$  in (1) we have  $n$  in terms of these other quantities. Differentiating with respect to  $p$  it is found that  $n$  is a maximum when

$$\frac{v}{lp_m} = NV,$$

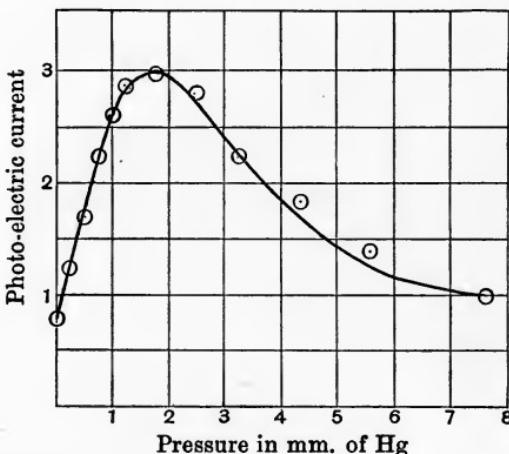
which is Stoletow's experimental relation. The maximum current at  $p_m$  is

$$n_m = n_0 e^{\frac{v}{Ve}}.$$

Hence the ionising potential  $V$  in terms of the maximum current  $n_m$ , the current in vacuo  $n_0$ , and the potential difference  $v$ , is

$$V = \frac{v}{e \log \frac{n_m}{n_0}}.$$

Partzsch<sup>1</sup> introduces a correction which makes the results agree much better with theory at low voltages. If  $v$  be the potential



The theoretical curve shown in the figure is for air.

$$v = 121.5 \text{ volt}; l = 208 \text{ cm.}; i_0 = .83.$$

The experimental values are indicated thus  $\odot$ .

Fig. 14.

difference, and  $V$  the ionising potential, then ionisation by collision occurs only in the section  $l \left(1 - \frac{V}{v}\right)$ . The alterations are

$$n = n_0 e^{al \left(1 - \frac{V}{v}\right)}, \quad n_m = n_0 e^{\frac{v-V}{Ve}},$$

$$V = \frac{v}{1 + e \log \frac{n_m}{n_0}}.$$

<sup>1</sup> Partzsch, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 60, 1912.

The curve (Fig. 14) gives the experimental relation between the current and the pressure and the corrected theoretical relation. The values of  $V$ , the ionising potential, obtained by Townsend and Partzsch are given in the following table :

	Partzsch	Townsend
Air	27.1 volts	25.0 volts
N <sub>2</sub>	27.9 „	27.6 „
O <sub>2</sub>	23.9 „	—
H <sub>2</sub>	27.8 „	26.0 „
CO <sub>2</sub>	23.5 „	23.3 „
HCl		16.5 „
H <sub>2</sub> O		22.4 „
A		17.3 „
He		14.5 „

These ionising potentials are considerably larger than those obtained by direct methods by Franck and Hertz, Lenard, and Dember. Not only are the magnitudes different from those given by direct methods, but in some cases the order is reversed as may be seen from Franck and Hertz's values, which are

He	Ne	Ap	H	O	N
20.5	16	12	11	9.0	7.5 volts

### *Proportionality between the Photo-Electric Current and the Light Intensity.*

Most theories of the nature of ionisation by light lead to definite relations between the number of electrons emitted and the intensity of the light. In particular, the photo-electric effect with very weak light has been investigated, as it is conceivable that, when the intensity falls below a certain small value, the photo-electric effect would diminish very rapidly or even perhaps cease altogether. It is known that photographic action ceases when the light intensity falls below a certain limit. If the product of the length of exposure and the intensity of the light be kept constant, then the blackening of the plate, which is constant over a wide range, falls off when the intensity is very weak. On the quantum theory of radiation in Einstein's form, the energy in the quantum is invariable and localized in an element of volume of unchanging size, and hence though the whole energy in the beam of

light may be very small, one would always expect a constancy between the intensity of the light (i.e. the number of quanta) and the photo-electric current. On certain resonance views, where the energy is accumulated until it reaches the amount  $hn$ , it is conceivable that a stage might be reached when the accumulation from the weak light is so slow, that it never overcomes dissipation in other directions to the extent necessary for the emission of a photo-electron.

Elster and Geitel<sup>1</sup> first showed that a proportionality existed between the photo-electric current from a potassium surface (in vacuo) and the intensity of the light. Lenard<sup>2</sup>, using a surface covered with soot, showed that a proportionality existed over a wide range. There was a proportionality even when the light intensity was reduced in the ratio  $1 : 10^6$  by reflection from a surface covered with soot. There was no indication of a smaller photo-electric effect with very weak light than was predicted by the proportionality law. Richtmyer<sup>3</sup> made some very accurate measurements, using sodium in vacuo as his photo-electric substance. He found a strict proportionality when the intensity of the light was varied from 600 to 0.007 foot candle power. Elster and Geitel<sup>4</sup> found that even when the light was so weak that the flow of energy was only about  $10^{-7}$  erg per sq. cm. per sec. and the photo-electric current about  $10^{-15}$  amp., there was no evidence of any departure from the proportionality law.

Apparent variations from proportionality can frequently be accounted for by spurious effects, usually fatigue or inverse fatigue effects. It seems quite conclusive that when disturbing effects are absent or allowed for, the relation between the total photo-electric current and the intensity of the light is a linear one. The experiments of Griffith<sup>5</sup> as to the relation between the photo-electric current and the light intensity are not in agreement with these results. However the evidence is overwhelmingly in favour of the linear relation.

Elster and Geitel<sup>6</sup> investigated the smallest amount of light

<sup>1</sup> Elster and Geitel, *Ann. d. Phys.* XLVIII. p. 627, 1893.

<sup>2</sup> Lenard, *Ann. d. Phys.* VIII. p. 149, 1902.

<sup>3</sup> Richtmyer, *Phys. Rev.* XXIX. p. 71, 1909; XXX. p. 385, 1910.

<sup>4</sup> Elster and Geitel, *Phys. Zeits.* XIII. p. 468, 1912.

<sup>5</sup> Griffith, *Phil. Mag.* XIV. p. 297, 1907.

<sup>6</sup> Elster and Geitel, *Phys. Zeits.* XIII. p. 468, 1912.

which would produce a measurable photo-electric effect. For this purpose they used a very sensitive potassium cell which had been treated by a glow discharge to increase its sensitiveness (p. 68). The presence of a small quantity of argon, in which ionisation by collision could be produced, in the cell enabled them to deal with currents which were 100 times larger than the current carried by the photo-electrons from the surface. The sensitiveness of this cell to blue light was not inferior to the human eye in its most sensitive condition. It was concluded that blue light imparting  $3 \times 10^{-7}$  erg per sec. per sq. cm. of the potassium surface produced a measurable photo-electric current of  $5 \times 10^{-15}$  amp. The exposed area of the metal was 12 sq. cm. and the number of electrons actually emitted from the surface was magnified 100 times. Hence to get the number of electrons emitted per sq. cm. we must divide by  $12 \times 100$ . Thus the total current carried away from 1 sq. cm. of the surface by the electrons is  $5 \times 10^{-15} \div 1200 = 4 \times 10^{-18}$  amp. Since the charge on an electron is  $1.55 \times 10^{-19}$  coulomb, this means that 26 electrons are emitted from 1 sq. cm. of the surface per second. Taking  $hn$  as the amount of energy associated with an electron released by light of frequency  $n$ , and putting

$$h = 6.55 \times 10^{-27}, \text{ and } n = c/\lambda = 3 \times 10^{10}/(4 \times 10^{-5}),$$

we get the energy per electron to be  $5 \times 10^{-12}$  erg. Hence the energy carried away by the 26 photo-electrons was  $1.3 \times 10^{-10}$  erg. But the amount of energy supplied in the beam of light was  $3 \times 10^{-7}$  erg, that is to say, only 2300 times greater than the energy associated with the liberated photo-electrons. Two things must be remembered. (1) Only a few of the photo-electrons emerge, the others are absorbed in the surface. (2) No account is taken of the reflected light, which makes the amount of absorbed light only a fraction of the incident light. The ratio of the energy of the photo-electrons actually *liberated in the surface* to that of the light *absorbed* is therefore considerably less than 2300. It seems clear then that we are getting near to a stage when the energy of the photo-electrons is not much less than that of the incident light<sup>1</sup>.

<sup>1</sup> With reference to this point, Pohl and Pringsheim (p. 87) mention that a potassium surface under certain conditions emits electrons whose total energy amounts to 2% or 3% of that of the light absorbed. Regarding the emerging

This has a very important bearing on the theory of the photo-electric effect. If the energy of the electron is derived from that of the light (and the wave fronts are continuous), then we should expect the energy of the photo-electrons to be of quite a different order from that of the light, since we may assume that the electron absorbs energy only from a part of the wave front whose area is comparable with the cross section of a molecule or from some still smaller area. As experiment suggests that the energies are of about the same order, it seems probable either that the energy in the wave front is localized as in Einstein's quantum theory, or that the light merely releases an electron with the energy it had in its orbit.

Marx and Lichtenecker<sup>1</sup> obtained results of the same order as Elster and Geitel's for the energy in the light beam necessary to produce the smallest detectable photo-electric current. In addition to this, they attacked the problem in another way. On certain resonance theories, time is required for the vibrating system to acquire energy from the light waves. The smaller the energy in the light wave, the longer is the time required. Hence it seemed possible that, on illuminating a photo-electric cell with weak light for very short periods, the photo-electric current would be smaller than that calculated from the proportionality law. A very sensitive potassium cell was illuminated by the light reflected from a revolving mirror. The total amount of light which fell on the cell per sec. was independent of the rate of rotation of the mirror, and hence, if the proportionality law holds, the photo-electric current should also be independent of the rate of rotation. By increasing the speed of the mirror the time of illumination could be cut down to  $10^{-7}$  sec. during which interval the surface was receiving energy at the rate of .56 erg per sq. cm. per sec. There was no departure from the proportionality law.

Marx<sup>2</sup> calculates the maximum energy which an electron, vibrating under the influence of a quasi-elastic force, can acquire electrons as only a fraction of the number released in the surface, we can safely conclude that the energy of the photo-electrons is of the same order as that in the incident light. Since the proportionality law is firmly established, these results may be taken as supporting the view advanced in the discussion above.

<sup>1</sup> Marx and Lichtenecker, *Ann. d. Phys.* xli. p. 124, 1913.

<sup>2</sup> Marx, *Ann. d. Phys.* xli. p. 161, 1913.

from a beam of light with a continuous wave front. The equation of motion of such an electron is, in Heaviside's units,

$$m \frac{d^2x}{dt^2} = -fx + \epsilon a e^{i2\pi nt} + \frac{\epsilon^2}{6\pi c^3} \frac{d^3x}{dt^3} \dots \dots \dots (3),$$

where  $n$  is the frequency and  $a$  the amplitude of the light wave,  $c$  the velocity of light,  $\epsilon$  the charge on an electron, and  $fx$  the quasi-elastic force acting on the electron at a distance  $x$  from its equilibrium position. The second term on the right-hand side is the electric force in the light wave acting on the electron. The third term is the damping force on the electron due to the radiation which it emits as its velocity changes.

The displacement of the electron at any time is  $x = b e^{i2\pi nt}$ . On substituting this in equation (3), and introducing the resonance condition  $f = m(2\pi n)^2$ , and taking the real part, we get

$$x = \frac{6\pi c^3}{\epsilon (2\pi n)^3} \cdot a \cos \left( nt - \frac{\pi}{2} \right) \text{ or } x = A \cos \left( nt - \frac{\pi}{2} \right).$$

The energy of the vibrating electron is

$$\begin{aligned} E &= \int_0^A f x dx \\ &= \frac{9}{4\pi^2} \cdot \frac{a^2}{2} \cdot \frac{m}{\epsilon^2} c^2 \lambda^4 \text{ erg} \dots \dots \dots (4), \end{aligned}$$

where  $c/n = \lambda$ . Now  $a^2/2$  is the energy of the light contained in unit volume and is equal to the energy falling on unit area per second divided by the velocity of light. Thus when .56 erg falls on unit area per second, as in the experiment last described, the energy density is  $.56/(3 \times 10^{10})$  erg per c.c. Substituting in (4) the values

$$\frac{a^2}{2} = \frac{.56}{3 \times 10^{10}}, \quad \lambda = 5 \times 10^{-5} \text{ cm.},$$

$$\frac{\epsilon}{m} = 1.77 \times 10^7 \times 3 \times 10^{10} \sqrt{4\pi}, \quad \epsilon = 4.69 \times 10^{-10} \sqrt{4\pi},$$

we get

$$E = 1.48 \times 10^{-17} \text{ erg.}$$

This is the greatest possible energy which an electron can

acquire from the light wave when its motion is represented by equation (3). Now we know that the energy of a photo-electron excited by light of frequency  $n$  is of the order  $hn$ , and for  $\lambda = 5 \times 10^{-5}$  cm. this works out to be

$$3.3 \times 10^{-12} \text{ erg.}$$

Marx therefore concludes that the photo-electron cannot possibly accumulate the necessary amount of energy from the light wave. He then suggests two ways out of the difficulty.

I. Assume that the vibrating electron does not lose energy by radiation and that therefore the equation of motion is equation (3) without the last term. Then it is possible for the photo-electron to acquire the necessary amount of energy from the light beam, even when the energy is distributed uniformly over the wave front. Such a system introduces a good many difficulties and it is doubtful whether the omission of the damping term is any gain.

II. Assume that the light is not distributed evenly over the wave front, but that there are places where there is exceptional concentration of energy. The number of photo-electrons emitted gives the number of concentration specks required and this number multiplied by the amount  $hn$  gives the total energy required for producing photo-electrons. This is only about one part in 10,000, or more, of the energy supplied. Hence to account for the photo-electric and optical experiments at the same time, Marx suggests that the wave surface may be regarded as a number of specks of concentrated energy distributed over a continuous background and that the total energy in the specks need only be .01% of the total energy. Lorentz<sup>1</sup> has put forward a view that the amplitude in a light wave is not uniform over the wave front but varies from place to place according to the law of probability. There would be very few regions in which the intensity is sufficiently great to communicate  $hn$  units of energy to an electron according to the motion contemplated in equation (3), and from this it would follow that the total energy of the photo-electrons is small compared with the energy in the incident light. These regions of great energy concentration correspond to the specks in Marx's

<sup>1</sup> Lorentz, *Phys. Zeits.* xi. p. 1250, 1910.

view. Marx's picture of a wave surface as specks of intense energy on a continuous background containing almost all the energy is built up on the experiments in which the total energy of the photo-electrons accounts for only about .01 % of the total energy in the incident light. The considerations we brought forward on p. 60, especially those referring to Pohl and Pringsheim's experiments, imply that, on Marx's view, the energy in the continuous background is only of the same order as that in the specks. To explain optical phenomena, it seems necessary that the energy in the specks should be negligible in comparison with that in the continuous background. Marx's dualistic conception of the structure of the wave front, which is only of use when almost all the energy is localized in the continuous background, does not seem adequate for explaining these results.

### *Applications to Radiometry.*

Several physicists have used photo-electric cells for energy measurements in radiometry and in doing so have assumed the linear relation between the photo-electric current and the light intensity. A photo-electric cell is in many cases quite as convenient to handle as a thermopile and a sensitive galvanometer, and moreover enables one to deal with light intensities of a far smaller order of magnitude. A thermopile will detect a flow of energy of the order  $10^{-1}$  erg per sq. cm. per sec., while according to Elster and Geitel's work the energy detectable by a photo-electric cell is  $10^{-7}$  erg per sq. cm. per sec. which is comparable with the sensitivity of the human eye. Photo-electric cells have been used by Nichols and Merritt<sup>1</sup> for the study of luminescence, by Richtmyer<sup>2</sup> for measuring rapidity of photographic shutters and decay of phosphorescence, by Elster and Geitel<sup>3</sup> for measuring light intensities during solar and lunar eclipses, and by Harms<sup>4</sup> for studying the changes of the intensities of light during a solar eclipse.

<sup>1</sup> Nichols and Merritt, *Phys. Rev.* xxiv. p. 471, 1907.

<sup>2</sup> Richtmyer, *Phys. Rev.* xxx. p. 394, 1910.

<sup>3</sup> Elster and Geitel, *Phys. Zeits.* xi. p. 212, 1910; xiii. p. 582, 1912.

<sup>4</sup> Harms, *Phys. Zeits.* vii. p. 585, 1906.

✓ *The Photo-Electric Effect and Temperature.*

The results of the earlier experiments on the change of photo-electric effect with temperature are very conflicting. The experiments were generally carried out in the presence of a gas which would ooze in and out of the surface of the metal as the temperature altered. We now know that the amount of gas occluded in the surface of a metal has a great influence on the photo-electric current apart from temperature changes. Zeleny<sup>1</sup> measured the photo-electric effect of Pt and Fe in air at different temperatures and found it to change with the temperature. The change in the photo-electric effect lagged behind the change in temperature which clearly indicates that the effect is due to the gas content of the surface slowly adjusting itself to equilibrium at different temperatures. Varley and Unwin<sup>2</sup> found big temperature changes in the photo-electric effect of Pt in different gases. In hydrogen, the effect increased rapidly with the temperature, in oxygen and CO<sub>2</sub>, the effect decreased as the temperature rose to about 400° and then started to increase. Final values at any temperature were only obtained after maintaining the Pt at that temperature for a considerable time. Elster and Geitel<sup>3</sup> found that the photo-electric effect of potassium in the presence of hydrogen at 3 mm. pressure increased 50% as the temperature changed from 20° to 50°. Sir J. J. Thomson (*Conduction of Electricity through Gases*, p. 285) found that when the temperature of the alkali metals was raised to about 200° a great increase in the photo-electric current was obtained.

On the other hand, Dember<sup>4</sup> investigated the effect in vacuo for K, Na, and K-Na alloy from room temperature up to 110° and found no change in the photo-electric current. This included a change from the solid to the liquid state in the case of K and Na. Varley and Unwin<sup>5</sup> repeated their experiments on the temperature effect of platinum in vacuo and found the effect to be

<sup>1</sup> Zeleny, *Phys. Rev.* xii. p. 321, 1901.

<sup>2</sup> Varley and Unwin, *Proc. Roy. Soc. Edinburgh*, xxvii. p. 117, 1907.

<sup>3</sup> Elster and Geitel, *Ann. d. Phys.* xlvi. p. 625, 1893.

<sup>4</sup> Dember, *Ann. d. Phys.* xxiii. p. 957, 1907.

<sup>5</sup> Varley and Unwin, *Proc. Roy. Soc. Edinburgh*, xxvii. p. 117, 1907.

independent of the temperature from  $60^\circ$  to  $350^\circ$ . Ladenburg<sup>1</sup> found the photo-electric current from Pt, Au and Ir (in vacuo) to be independent of the temperature up to  $800^\circ$ . Millikan and Winchester<sup>2</sup> found that the photo-electric current from Au, Ni, Ag, Fe, Mg, Sb, Zn, and Pb in vacuo was independent of the temperature over a range from  $15^\circ$  to  $125^\circ$ .

We can conclude from these experiments, and those described on p. 42, that the magnitude of the photo-electric effect and the velocity of the photo-electrons are alike independent of the temperature of the illuminated plate. When there is an apparent change with the temperature, this may safely be attributed to some secondary effect of the temperature, such as a change in the amount of gas absorbed, rather than to the fundamental photo-electric action.

If the photo-electrons were originally the free electrons which take part in electrical conductivity and in thermionic effects, one might expect that it would be easier for the light to cause the emission of the electrons at higher temperatures. At the higher temperatures there are more electrons moving towards the surface with velocities sufficient to make it an easy matter to pull them through. It is more probable that the photo-electron comes from the molecule, in which the forces tending to keep the electron inside vary either very slowly, or not at all, with the temperature.

### *The Effect of an Electric Discharge on Photo-Electric Sensitiveness.*

It is well established now that using a metal as an electrode in an electric discharge at low pressures alters the gas content of the surface. Since we know from fatigue and other experiments that the amount of occluded gas affects the photo-electric sensitiveness of a metal, we should therefore expect that treating a metal as an electrode in a discharge would have a marked effect on the photo-electric current emitted by it. Such is the case. The processes in the discharge are, however, so complex, and so many factors come in to an unknown extent, that it is not surprising that the experimental results are conflicting.

Holman<sup>3</sup> investigated the effects of using Zn, Cu, Ag, Al, and

<sup>1</sup> Ladenburg, *Verh. d. Deutsch. Phys. Ges.* ix. p. 165, 1907.

<sup>2</sup> Millikan and Winchester, *Phil. Mag.* xiv. p. 188, 1907.

<sup>3</sup> Holman, *Phys. Rev.* xxv. p. 81, 1907.

Fe as electrodes in a hydrogen discharge. After using the metals as cathodes, the sensitiveness increased; after using them as anodes, the sensitiveness decreased, the order of the change being 6 to 1 in the case of zinc. Holman refers to Skinner's work in which cathodes emit hydrogen and anodes absorb it. Holman's results indicate therefore that the less the amount of occluded hydrogen, the greater the photo-electric sensitiveness. Chrisler<sup>1</sup> obtained quite different results with a large number of metals. The sensitiveness was greater after use as anode than after use as cathode in hydrogen. When other gases were used, he obtained the reverse effect, viz. a decrease in sensitiveness after use as anode. Consequently he suggested that if the hydrogen could be completely removed, the photo-electric effect might vanish. Experiments of this kind are unsatisfactory in that it is extremely difficult to control the various factors which are introduced by the discharge. Skinner's work is quoted as indicating that a metal absorbs hydrogen when acting as anode in a glow discharge. But we also know that when the pressure is sufficiently low to allow the cathode rays to strike the anode, then hydrogen and other gases are driven out of it. Thus slight differences in the conditions under which the discharge takes place may produce quite different effects. Both Holman and Chrisler used induction coils, and very probably the discharge was not uni-directional. A high potential battery would have avoided the possible trouble arising from reversals.

Wulf<sup>2</sup> found that charging a sheet of platinum electrolytically with hydrogen increased the photo-electric current from it about ten times. A positively charged layer on the surface of a metal would assist, and a negatively charged layer would retard, the emission of photo-electrons. Such layers are undoubtedly formed on electrodes in discharge tubes, and in liquids, as Wulf's result indicates. The velocity experiments with metals treated as electrodes support this view, for after using the metal as a cathode, extremely high emission velocities can be obtained.

We shall now turn to certain changes produced by cathode rays in the photo-electric sensitiveness of certain substances.

<sup>1</sup> Chrisler, *Phys. Rev.* xxvii. p. 267, 1908.

<sup>2</sup> Wulf, *Ann. d. Phys.* ix. p. 946, 1902.

Elster and Geitel<sup>1</sup> found that the halogen salts of the alkali metals and some other salts, such as  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{K}_2\text{CO}_3$ , when coloured by bombardment with cathode rays, were extremely sensitive photo-electrically to visible light. (The salts before colouring are quite insensitive, even to ultra-violet light.) Elster and Geitel explain the colouring as being due to free alkali metal dissolved in the salt, the whole forming a solid solution.

Later Elster and Geitel<sup>2</sup> converted the alkali metals into hydrides by heating them in hydrogen at a temperature of about  $350^\circ$ . The hydrides were in the form of clear colourless crystals and were quite insensitive to visible light. On bombarding the hydrides with cathode rays, large quantities of hydrogen were evolved and the hydrides became brightly coloured. The colours were blue-violet for K, the same, but paler, for Rb, green for Cs, and brown for Na. The photo-electric sensitiveness of these coloured surfaces was from 3 to 4 times greater than that of the corresponding pure metals. Elster and Geitel regard these coloured substances as the alkali metals in a colloidal state dissolved in the solid hydride. (The colouring is probably caused in the same way as that of glasses stained with metallic oxides.) To get the colloidal modification, it is unnecessary to convert the metal into the hydride as a preliminary step. The amount of hydride can be so small that one may regard the substance as a pure colloidal modification of the metal. A glow discharge in rarefied hydrogen in contact with the ordinary pure metal will give the colloidal modification. Very small amounts of hydrogen will enable the change from the ordinary form to the colloidal form to take place. To get the greatest possible sensitiveness to light, it is necessary to leave a little gas in the cell so that the effect may be magnified by ionisation by collision. In the course of time, however, the hydrogen in these cells containing the colloidal metals disappears and at the same time the colour fades and the photo-electric sensitiveness falls off. The hydrogen probably combines with the colloidal metal. This can be avoided and a cell of a permanent type can be made by substituting argon or helium for the hydrogen after the colouring has been produced<sup>3</sup>.

<sup>1</sup> Elster and Geitel, *Ann. d. Phys.* lix. p. 487, 1896.

<sup>2</sup> Elster and Geitel, *Phys. Zeits.* xi. pp. 257, 1082, 1910.

<sup>3</sup> Elster and Geitel, *Phys. Zeits.* xii. p. 609, 1911.

With a cell containing colloidal potassium, Elster and Geitel<sup>1</sup> could detect the infra-red rays which passed through ebonite .97 mm. thick. The effect apparently falls off gradually with increase of the wave-length, no sudden cessation being observed.

These cells are admirably adapted for detecting very weak radiation. The sensitiveness is a maximum at  $\lambda 3200$ ,  $\lambda 4400$ ,  $\lambda 4800$  and (probably)  $\lambda 5500$  for Na, K, Rb and Cs respectively (Pohl and Pringsheim, and Lindemann<sup>2</sup>). When the best conditions for the gas pressure are obtained and a suitable potential producing a large amount of ionisation by collision is used, these cells can detect extraordinarily small amounts of light. Kemp<sup>3</sup> calculates that a cell he used would give a measurable current of  $10^{-15}$  amp. when illuminated by a candle at 2·7 miles. Elster and Geitel<sup>4</sup> find that their cells (of K) are not inferior to the human eye in sensitiveness, especially in the blue end of the spectrum.

Pohl and Pringsheim<sup>5</sup> suggest that the increased sensitiveness of the colloidal modification is due to the greater ease with which the electrons can emerge from the tiny globules of metal which characterize the colloidal state. The average diameter of these globules is probably considerably less than  $10^{-5}$  cm. Let  $d$  (Fig. 15) be the distance through which the electron can penetrate. For a smooth coherent surface the ratio of those which emerge to those produced at  $O$  is of the order of the solid angle  $\omega$  to  $4\pi$ . But if a globule of radius  $d$  had its centre at  $O$ , then all the electrons could emerge. Bigger globules would behave in a way intermediate between the small globule considered and the flat surface. On these lines, Pohl and Pringsheim account for the greater sensitiveness of a surface composed of a large number of tiny globules as compared with ordinary coherent surfaces.

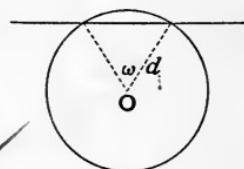


Fig. 15.

<sup>1</sup> Elster and Geitel, *Phys. Zeits.* xii. p. 758, 1911.

<sup>2</sup> Lindemann, *Verh. d. Deutsch. Phys. Ges.* xiii. p. 482, 1911.

<sup>3</sup> Kemp, *Phys. Rev.* (2) i. p. 273, 1913.

<sup>4</sup> Elster and Geitel, *Phys. Zeits.* xiii. p. 468, 1912.

<sup>5</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xiii. p. 211, 1911; xv. p. 179, 1913.

### Photo-Electric Fatigue.

It has long been known that the photo-electric sensitiveness of a recently exposed metallic surface decreases with the time. This phenomenon is called photo-electric fatigue. It has been accounted for in many ways, e.g. oxidation of the surface, effect of illumination, changes in the electrical double layer at the surface, absorption of the surrounding gas by the metal, presence of an electric field assisting or retarding the photo-electric current, and mechanical alteration of the surface. We shall consider separately the fatigue in the presence of a gas at atmospheric pressure and the fatigue in vacuo.

#### Fatigue in the Presence of a Gas.

Hallwachs<sup>1</sup> found that the fatigue progressed at the same rate whether the metal was illuminated or not. Neither did the presence of an electric field, assisting or retarding the photo-electric current, have any effect on the rate of fatigue. Illumination sometimes appears to produce a fatigue, but this is due to the formation of ozone by ultra-violet light which is the real cause of the fatigue. The evidence against the oxidation theory is that the initial sensitiveness and consequent fatigue is much the same in Cu, CuO, and Cu<sub>2</sub>O. This also applies to Pb and PbO<sub>2</sub>. The photo-electric fatigue of platinum was investigated simultaneously with changes in the contact potential. There was no quantitative relation between the two effects. Frequently treatment which produced strong fatigue had scarcely any effect on the contact potential and vice versa. From this, Hallwachs concluded that variations in the electrical double layer were not the cause of fatigue. However, the direction of the change in both phenomena was nearly always the same (fatigue and increase of electro-negative character usually run together), and it appears probable that both effects are the result of some common cause. Allen<sup>2</sup> supports Hallwachs in rejecting these explanations of fatigue.

Hallwachs pointed out that the rate of fatigue is very much

<sup>1</sup> Hallwachs, *Ann. d. Phys.* xxiii. p. 459, 1907.

<sup>2</sup> Allen, *Proc. Roy. Soc. A.* lxxviii. p. 489, 1906; *Phil. Mag.* xx. p. 564, 1910.

greater when the metal plate is exposed to the free air of a room than when it is confined in a small vessel. A freshly cleaned copper plate fatigued to .33 of its original value in the course of a day when exposed in a room. To effect the same fatigue in a closed vessel, containing air at atmospheric pressure, required three months. The open air fatigue is attributed to the presence of traces of ozone which produces a powerful fatigue agent. The introduction of ozone into a vessel containing a zinc plate (Ullmann<sup>1</sup>), and a copper plate (Hallwachs, *l.c.*), produced a very marked fatigue, which however almost entirely disappeared on removing the ozone. From the temporary character of the fatigue it was concluded that ozone does not produce oxidation. Hallwachs (*Congrès International de Radiologie*, Brussels, p. 642, 1910) suggests that the fatigue agent is  $H_2O_2$  produced by ozone and moisture. He found that  $H_2O_2$  has an enormous absorption for ultra-violet light and hence a very thin film over the metal surface would reduce the intensity of the light very considerably. Similar differences between the fatigue in the open air and in a vessel have been investigated by Allen<sup>2</sup>.

The rate of fatigue of Cu, CuO and Pt kept in air in closed vessels is given in the following table (Hallwachs):

Time	Photo-Electric Sensitiveness		
	Cu	CuO	Pt
0 months	100	100	100
3 "	31	64	94
6 "	33	60	82
9 "	31	54	63
12 "	28	44	57
18 "		38	—
30 "		32	50

Hallwachs attributed this fatigue to the slow absorption of gases by the surface. The gases either absorb some of the light which produces a photo-electric effect, or retard the escape of

<sup>1</sup> Ullmann, *Ann. d. Phys.* xxxii. p. 1, 1910.

<sup>2</sup> Allen, *Phil. Mag.* xx. p. 564, 1910.

electrons. This view is supported by the fact that the sensitiveness of Pt at ordinary temperatures is greater after being heated and less after being cooled. In the first case, heat drives off some of the gas and hence the photo-electric sensitiveness is above its equilibrium value ; in the second case, the surface absorbs more gas and only gets rid of it slowly at ordinary temperatures. The most reliable way of getting a Pt plate to give constant initial values is to make it red-hot. It may be assumed, after such treatment, that the occluded gases which give rise to the fatigue have been driven off.

Ullmann<sup>1</sup> found that the fatigue is much more rapid with Zn than with Cu. While the presence of water vapour has but little effect on the fatigue of Cu, it increases the rate of fatigue of Zn. Becker<sup>2</sup>, contrary to Ullmann, finds that water vapour has the power of arresting the fatigue which once more proceeds on removal of the water vapour.

Allen<sup>3</sup> found for Zn, and Hallwachs for Cu and Pt, that the fatigue was of the same order in hydrogen as in air.

Ullmann discovered that the initial sensitiveness of a plate, as distinct from its fatigue, depended largely on the surrounding atmosphere. He obtained the following values for a zinc plate.

Atmosphere	Photo-Electric Sensitiveness		Dielectric Capacity
	Dry gas	Wet gas	
H <sub>2</sub>	1·00	2·52	2·6 × 10 <sup>-4</sup>
air	2·94	8·10	5·9 „
CO <sub>2</sub>	7·30	17·40	9·8 „

In a recent paper, Hallwachs<sup>4</sup> puts forward the view that there is some relation between the photo-electric sensitiveness and the dielectric capacity of the gas in contact with the surface. Experiments with NH<sub>3</sub> support this view, experiments with organic vapours are indecisive. Hallwachs now suggests that some

<sup>1</sup> Ullmann, *Ann. d. Phys.* xxxii. p. 1, 1910.

<sup>2</sup> Becker, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 806, 1912.

<sup>3</sup> Allen, *Phil. Mag.* xx. p. 564, 1910.

<sup>4</sup> Hallwachs, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 634, 1912.

absorption of gas by a metal is necessary before it will give a photo-electric effect at all. If this function is assigned to the absorbed gas, it seems necessary to look elsewhere for the cause of fatigue. One cannot see from the theoretical standpoint how the dielectric capacity of the gas can influence the photo-electric effect of the metal.

Bergwitz<sup>1</sup> showed that there was no fatigue with cells containing Na, K, and Rb in the presence of H<sub>2</sub> at 3 mm. pressure. The period of investigation never exceeded a few hours.

Allen<sup>2</sup> found that the photo-electric effect of iron was from 10 to 20 times less when it was in the "passive" state than when in the "active" state. Modern chemical research attributes the "passivity" of metals to the formation of an imperceptible surface layer of oxide protecting the pure metal beneath<sup>3</sup>. Thus one would expect passivity to be accompanied by a great decrease in the photo-electric effect.

### Fatigue in vacuo.

A number of researches have been carried out on the photo-electric fatigue in vacuo. This term is only justified when we are satisfied that the pressure of the residual gas is too small to have any appreciable effect on the phenomenon under investigation. That a very small amount of residual gas is sufficient to affect the photo-electric sensitiveness of a plate is suggested by the conflicting results of experiments carried out at low pressures. Ladenburg<sup>4</sup> found that Al showed no fatigue in vacuo while Ag did. Dember<sup>5</sup> found that the sensitiveness of a Na-K cell remained constant for 12 months. The Na cells used by Richtmyer<sup>6</sup> showed no fatigue. Millikan and Winchester<sup>7</sup> found there was no fatigue in vacuo for the eleven metals tested. That fatigue does not occur in

<sup>1</sup> Bergwitz, *Phys. Zeits.* VIII. p. 373, 1903.

<sup>2</sup> Allen, *Proc. Roy. Soc. A.* LXXXVIII. p. 70, 1913.

<sup>3</sup> Grube, *Zeits. f. Elektrochemie*, p. 189, 1912; Isgarischew, *Zeits. f. Elektrochemie*, p. 491, 1913.

<sup>4</sup> Ladenburg, *Ann. d. Phys.* XII. p. 538, 1903.

<sup>5</sup> Dember, *Ann. d. Phys.* XXIII. p. 957, 1907.

<sup>6</sup> Richtmyer, *Phys. Rev.* XXX. p. 394, 1910.

<sup>7</sup> Millikan and Winchester, *Phil. Mag.* XIV. p. 188, 1907.

permanently sealed cells is supported by the fact that such cells are now regarded as reliable instruments for measuring light intensity.

On the other hand a number of investigators have observed fatigue in vacuo. Allen<sup>1</sup> and Hallwachs found fatigue in Zn and Cu respectively. Robinson<sup>2</sup> observed fatigue effects with Zn and Al. According to his experiments, the fatigue occurs only after the illuminated plate has been emitting electrons; if they are prevented from escaping by a suitable field, then no change is observed. Herrmann<sup>3</sup> found that new surfaces of Ag, Pt, Sn, Pb, Al and Mg, exposed in vacuo by scraping with a steel tool, showed marked fatigue. The pressure was less than .0001 mm. Herrmann suggests that the effect is due to the formation of H<sub>2</sub>O<sub>2</sub> from traces of moisture by the ultra-violet light.

On considering these investigations as to the presence or absence of fatigue in vacuo, two well-marked facts appear. In the case of the alkali metals, they are studied in glass cells with platinum sealed electrodes, so that there is no chance of any leak. There is no evidence as to how soon the cells were tested after being made. One may presume that some hours elapsed, and so it may be considered that the surfaces had attained a state of equilibrium. But it is significant that in the experiments which showed fatigue, waxed joints, taps, etc., were essential parts of the apparatus, and so there was more chance of traces of vapours and gases finding their way into the apparatus. Again, experiments were usually carried out soon after treating the surface, and hence a re-adjustment of the absorbed gases in the metal was no doubt still taking place.

In spite of the fact that photo-electric fatigue has perhaps been more investigated than any other branch of photo-electricity, its nature is still obscure. It seems clear that fatigue is connected in some way with the variations in the amount, and the kinds, of occluded gases or vapours, but as to how these act there is no direct evidence. It does not seem likely at present that experiments on fatigue will give any information as to the fundamental

<sup>1</sup> Allen, *Proc. Roy. Soc. A.* LXXVIII. p. 489, 1906.

<sup>2</sup> Robinson, *Phil. Mag.* xxiii. p. 255, 1912.

<sup>3</sup> Herrmann, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 557, 1912.

processes of photo-electricity. Possibly when more is known about the emission and absorption of photo-electrons, experiments on photo-electric fatigue will go some way towards elucidating the problems of absorption of gases by metals.

### *Photo-Electric Effect of Alloys.*

Euchen and Gehloff<sup>1</sup> investigated the electrical conductivity of alloys containing different proportions of antimony and cadmium. The conductivity of the alloys deviated in a very marked manner from that calculated on the assumption that each metal contributed to the conductivity in proportion to its amount in the alloy. The result suggested to Herrmann<sup>2</sup> the desirability of testing the same alloys photo-electrically. It was found that the photo-electric effect of any alloy was intermediate between the effects of the constituent metals and varied linearly with the amount of either metal in the alloy.

From one point of view, this result suggests that the photo-electrons are not the free electrons involved in electrical conductivity. But one should bear in mind that the abnormal conductivity of these alloys probably arises from thermo-electric effects between the minute crystals of the different metals in the alloy. (See Sir J. J. Thomson, *Corpuscular Theory of Matter*, p. 59.) So far as the photo-electric effect is concerned, each crystal should give its own effect characteristic of the metal and thus the photo-electric effect of the alloy would be directly determined by the composition of the alloy.

Some remarkable experiments have been published very recently by Pohl and Pringsheim<sup>3</sup> on the photo-electric effect of alloys of mercury and potassium. The results do not agree at all with those given above. In Fig. 16, the curve I refers to the photo-electric effect of pure mercury while the curves II to V refer to the alloys. The photo-electric effect of the alloys is of the same order as the normal effect for potassium and only decreases about 30% even when the percentage of potassium changes from 2·3 to

<sup>1</sup> Euchen and Gehloff, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 169, 1912.

<sup>2</sup> Herrmann, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 573, 1912.

<sup>3</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xv. p. 431, 1913.

$2 \times 10^{-4}$ , a range of  $10^4$  to 1. The long wave-length limit of the effect shifts only very slowly as the amount of potassium decreases. One obvious difference between these experiments and those of Herrmann is that Herrmann's alloys were solid while these are

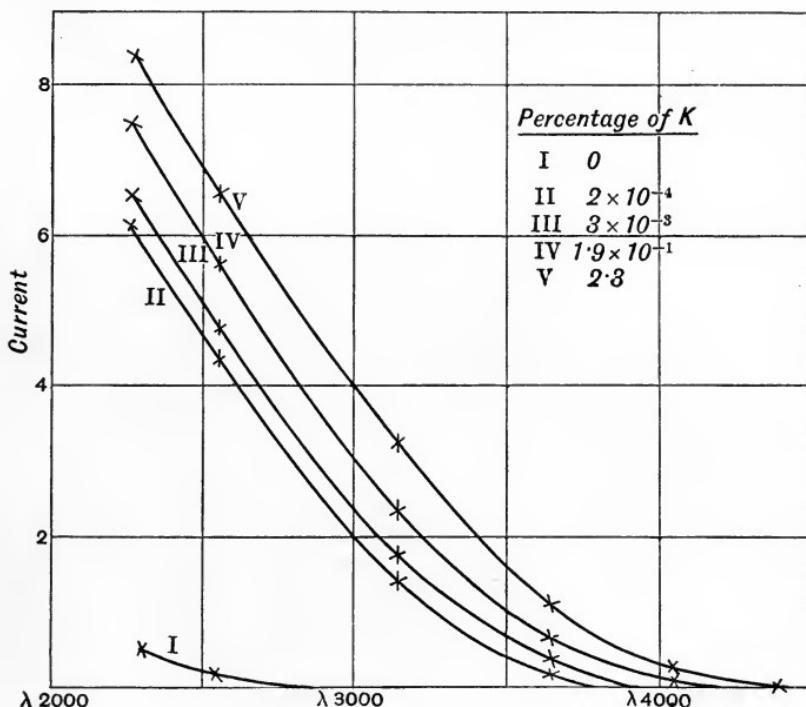


Fig. 16.

liquid. The results suggest that the potassium is concentrated in the surface of the alloys, though there are no other grounds at all for believing that such is the case. Further experiments on the photo-electric effect of alloys are required before any adequate explanation can be offered.

## CHAPTER V

### THE PHOTO-ELECTRIC EFFECT AS A FUNCTION OF THE FREQUENCY AND STATE OF POLARISATION OF THE LIGHT

LADENBURG<sup>1</sup> investigated the relation between the photo-electric effect and the energy in the incident light for different wave-lengths. He found that the photo-electric sensitiveness, using this term to denote the photo-electric current per unit intensity of the incident light, increased rapidly with decreasing wave-length for Pt, Cu, and Zn. The results for these metals are shown in Fig. 17. Similar results were obtained by Mohlin<sup>2</sup>. Experiments have shown that there is a great difference between the alkali metals and other metals in the way in which their photo-electric sensitiveness depends upon the wave-length of the light. As the wave-length decreases, the photo-electric sensitiveness of each alkali metal reaches a maximum at a particular wave-length and then diminishes again. The alkali metals possess still another peculiarity; the sensitiveness depends very much upon the state of polarisation of the light.

In such experiments it is necessary to have a very smooth

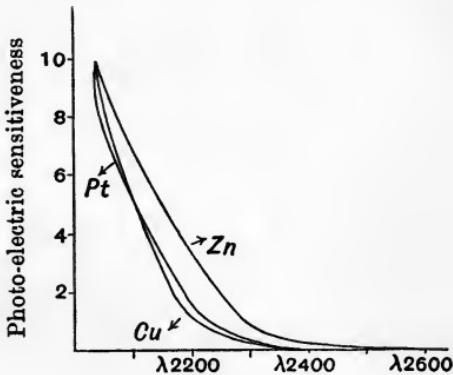


Fig. 17.

<sup>1</sup> Ladenburg, *Verh. d. Deutsch. Phys. Ges.* ix. p. 166, 1907.

<sup>2</sup> Mohlin, *Akad. Abhandl. Upsala*, 1907.

surface, otherwise the plane of polarisation relative to the surface will have little meaning. Failure to use a sufficiently smooth surface probably accounts partly for the discrepancies between some of the earlier and the later experiments on the effects of polarisation. Thus Ladenburg<sup>1</sup> found that the photo-electric current from polished steel did not depend upon the state of polarisation of the light. Elster and Geitel<sup>2</sup> were the first to make experiments on the variation of the photo-electric current with the state of polarisation of the light. A smooth surface was furnished by the liquid alloy of sodium and potassium, and was illuminated by white light striking the surface at an angle. We shall refer to the plane of polarisation parallel to the plane of incidence as the  $E \perp$  plane and to the plane of polarisation at right angles to this as the  $E \parallel$  plane. In terms of the Electro-magnetic Theory of Light,  $E$  denotes the electric force and the sign after it denotes the relation of the force to the plane of incidence. It was found that when the light was polarised in the  $E \parallel$  plane, the photo-electric effect was greater than when the light was polarised in the other plane. On varying the obliquity of the incident beam, it was found that the photo-electric current was proportional to the amount of light absorbed when the light was polarised in the  $E \perp$  plane; but when the light was polarised in the  $E \parallel$  plane, giving a much bigger photo-electric current, the current was not proportional to the amount of light absorbed. If however we consider only the energy corresponding to the component of the electric force at right angles to the surface, then there is a proportionality between this part of the energy absorbed and the photo-electric current, the small fraction of the current corresponding to the other component being subtracted.

With an angle of incidence of  $60^\circ$ , the photo-electric currents from the sodium-potassium alloy were as 117 to 2 when the light was polarised in the  $E \parallel$  plane and in the  $E \perp$  plane respectively.

Elster and Geitel<sup>3</sup> obtained the important experimental result that the maximum emission velocities of photo-electrons did not

<sup>1</sup> Ladenburg, *Ann. d. Phys.* xii. p. 558, 1903.

<sup>2</sup> Elster and Geitel, *Ann. d. Phys.* lii. p. 433, 1894; lv. p. 684, 1895; lxi. p. 445, 1895.

<sup>3</sup> Elster and Geitel, *Phys. Zeits.* x. p. 457, 1909.

depend upon the plane in which the light was polarised. But complete identity in the velocities was not established, for, on the whole, the electrons appeared to be slower when the light was polarised in the  $E \parallel$  plane. But for reasons similar to those discussed on p. 33, their experiments were not adapted to obtain conclusive evidence that the distribution of velocities amongst the electrons emitted depends upon the state of polarisation of the light. To take an extreme case, suppose that light polarised in the  $E \parallel$  plane causes the emission of electrons normally from the surface, while light polarised in the other plane causes the electrons to be emitted in all directions. Even if the real distribution of velocities were the same in both cases, the apparent distribution of velocities given by Elster and Geitel's method would be different.

Braun<sup>1</sup> found that K and Rb were most sensitive to  $\lambda 4400$  and  $\lambda 5100$  respectively.

Hallwachs<sup>2</sup> found, on the other hand, that the photo-electric sensitiveness of K increased steadily as the wave-length became shorter. In Hallwach's experiments, the incidence was normal and hence there could be no component of the electric force in the light beam perpendicular to the surface.

Much of the confusion in this branch of photo-electricity has been cleared up by the elaborate and systematic investigations of Pohl and Pringsheim, and now we possess some very clear and precise experimental information as to the relation between the total photo-electric current, the wave-length and the state of polarisation of the light for a considerable number of metals and some alloys.

Pohl<sup>3</sup> investigated the relation between the photo-electric currents from surfaces of Pt, Cu, and Hg and the state of polarisation of the light. To obtain metallic surfaces of Pt and Cu, which are so smooth that they possess no irregularities of dimensions comparable with the wave-lengths used, thin films were sputtered from suitable cathodes on to polished glass or quartz plates. In Fig. 18, the relation between the photo-electric current

<sup>1</sup> Braun, *Dissertation*, Bonn, 1906.

<sup>2</sup> Hallwachs, *Ann. d. Phys.* xxx. p. 593, 1909.

<sup>3</sup> Pohl, *Verh. d. Deutsch. Phys. Ges.* x. pp. 339, 609, 715, 1909.

and the angle of incidence of the light is given. When unpolarised light was used, the dotted line was obtained. This is similar to the curve obtained by Ladenburg<sup>1</sup> which indicates that, in his experiments, the surface was in reality rough when considered in relation to the order of the wave-lengths used, and consequently the polarisation of the light had little meaning relative to the surface. The amount of light absorbed was obtained from Drude's formulae, and the constants of Minor and Voigt.

$$L_{\perp} = \frac{4n \cos \psi}{n^2(1+k^2) + 2n \cos \psi + \cos^2 \psi},$$

$$L_{\parallel} = \frac{4n \cos \psi}{n^2(1+k^2) \cos^2 \psi + 2n \cos \psi + 1},$$

where  $n$  is the refractive index,  $k$  the absorption index and  $\psi$  the

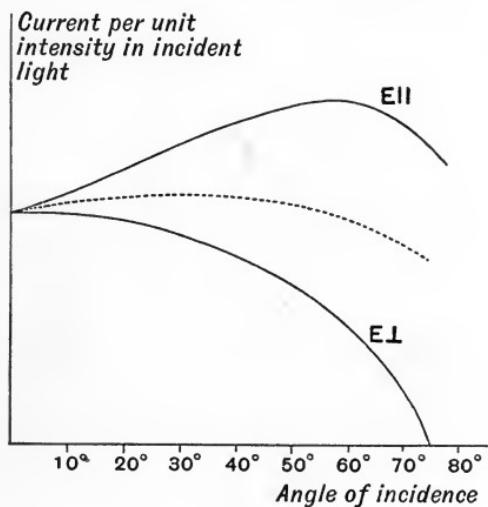


Fig. 18.

angle of incidence. If  $I_{\perp}$  and  $I_{\parallel}$  be the respective photo-electric currents, the ratios  $I_{\perp}/L_{\perp}$  and  $I_{\parallel}/L_{\parallel}$  are found to be the same for all angles of incidence. Hence it appears conclusive that, in the case of Pt, Cu, and Hg, the photo-electric current is proportional to the amount of light absorbed and depends only upon the state of polarisation of the light to the same degree as the absorption does. The emission velocities of the photo-electrons were unaltered as the plane of polarisation was rotated.

<sup>1</sup> Ladenburg, *Verh. d. Deutsch. Phys. Ges.* ix. p. 166, 1907.

Pohl and Pringsheim investigated for the alkali metals the relation between the photo-electric current and the wave-length and the state of polarisation of the incident light<sup>1</sup>. Their results have finally accounted for the contradictory results previously obtained. In Fig. 19, a typical curve for Na-K alloy illuminated obliquely by polarised monochromatic light is given. Abscissae show the wave-lengths and ordinates the photo-electric current per unit intensity in the incident light beam. When the light

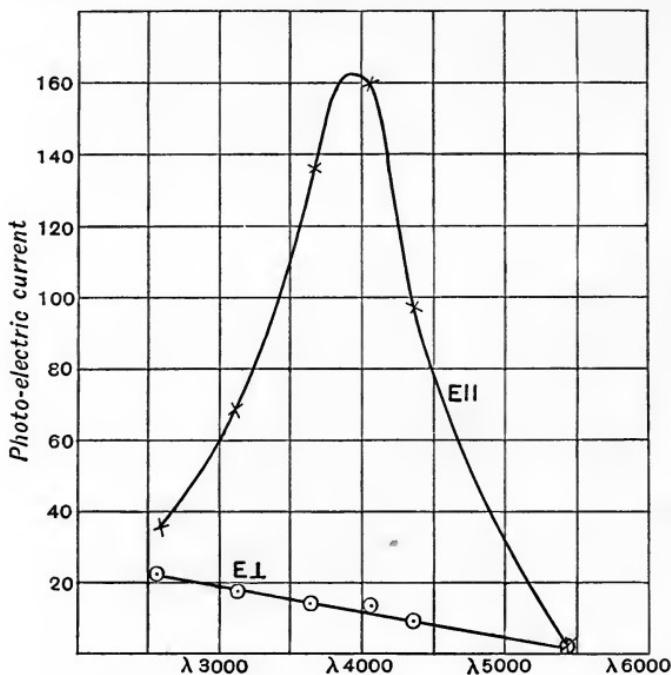


Fig. 19.

Selective and normal effects for Na-K alloy.

is polarised in the  $E \perp$  plane, the photo-electric effect increases rapidly and continuously with decreasing wave-length. When however the light is polarised in the  $E \parallel$  plane, a very different curve is obtained. This may be regarded as the superposition of two curves, one similar to the  $E \perp$  curve and the other similar to the curves of Fig. 20. The former component (that similar to the  $E \perp$  curve) can be deduced when the proportion of the energy in the incident beam corresponding to the component of the electric

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xii. p. 215, 1910.

force perpendicular to the plane of incidence is known. A maximum in the curve does not appear when the incidence is normal, for then the electric force in the light has no component perpendicular to the surface, but as the angle of incidence increases, this peculiarity in the curve becomes more and more pronounced. This is quite evident from Fig. 20 which gives the selective effects after subtracting the normal effects for different angles of incidence<sup>1</sup>.

Thus the photo-electric effect in the alkali metals may be regarded (as by Pohl and Pringsheim) as the superposition of two

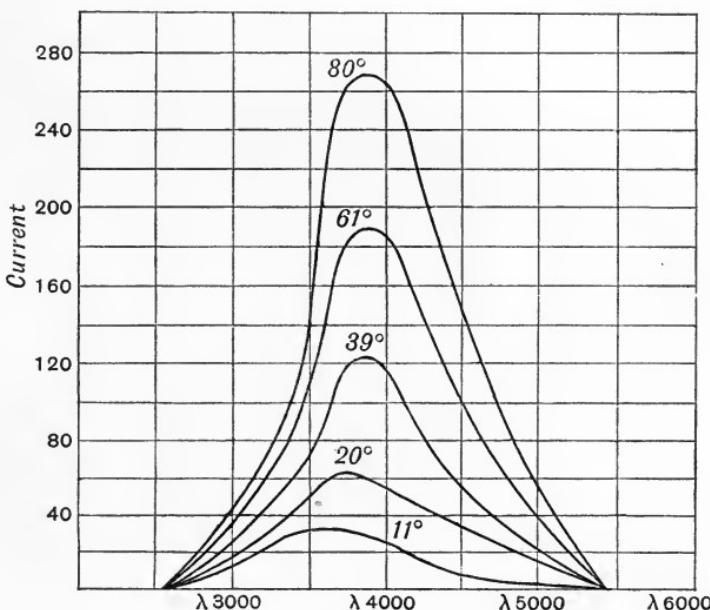


Fig. 20.

Selective effect for Na-K alloy with different angles of incidence.

distinct effects, the "normal" effect and the "selective" effect. The "normal" photo-electric effect increases with decreasing wavelength and does not depend on the state of polarisation of the light except in so far as this affects the amount of light absorbed. The "selective" photo-electric effect is that part of the total photo-electric effect which appears when the light is polarised in the  $E \parallel$  plane and then only over a limited range of wave-lengths. The number of electrons liberated in the selective effect by unit

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xii. p. 682, 1910

energy in the light is much greater than in the normal effect. All metals possess a normal effect, the selective effect has only been shown to exist for a few metals mainly of the alkali group.

It is not convenient to use polarised light except with the liquid alloy of sodium and potassium, as it is almost impossible to get surfaces of the solid alkali metals of sufficient smoothness. This does not cause much trouble, however, for the effect can be studied with unpolarised light. The selective effect is so marked that it shows up well on the curve. The curve for rubidium with unpolarised light is given in Fig. 21. (In view of later experiments (p. 86) by Pohl and Pringsheim it is well to note that the presence

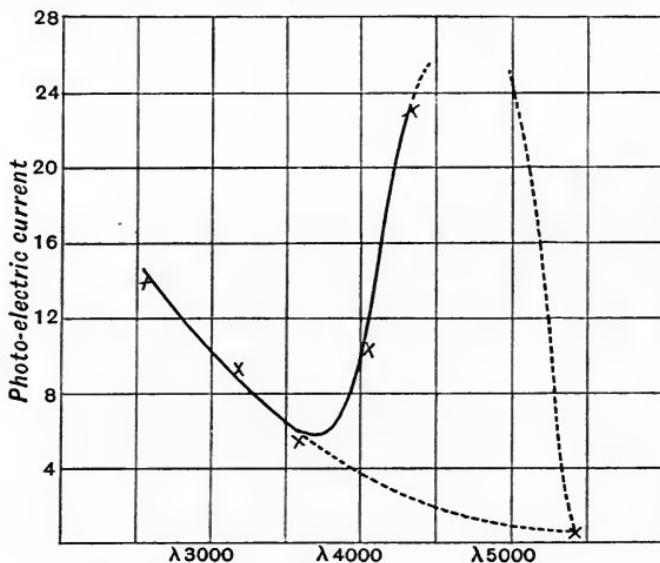


Fig. 21.

Rubidium. Normal and selective photo-electric effects superposed.

of a maximum in the curve is not in itself sufficient to show the existence of a selective effect.) The position of  $\lambda_{\text{max.}}$ , the wavelength at which the selective effect is a maximum, shifts towards the ultra-violet as the atomic weight of the alkali metals decreases. At the same time, the magnitude of the selective effect becomes less and the curve representing it becomes broader. The following table gives a summary of the positions and breadths of the selective regions for some metals and alloys<sup>1</sup>.

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xi. p. 1039, 1910.

Metal	$\lambda_{\max.}$	Breadth of the selective region
Rb	4700	1800
K	4400	2500
K-Na alloy	3900	2900
K-Hg alloy	3800	2900
Na	3400	$\Delta$ 3200
K-Tl alloy	3000	>3200
Li	2800	—
Ba	2800	—

While the position of  $\lambda_{\max.}$  remains constant for any one metal, the ratio of the selective effect to the normal effect varies enormously in different cells containing the same metal. With one cell (Na-K alloy), the selective effect was 300 times the normal effect, and frequently ratios of 10 or 15 to 1 were obtained. A cell used by Elster and Geitel gave a ratio of 50 to 1. The angle of incidence was always 60°.

When potassium was made into an alloy by the addition of other metals, there was a marked change in the selective effect and in many cases it disappeared<sup>1</sup>. The alloy which was investigated in most detail was that of potassium and mercury. It appears that the act of adding mercury to potassium is, first to reduce the selective effect and to shift it towards the ultra-violet, while the normal effect ends at about the same wave-length, and then when the selective effect has disappeared, to shift the limit of the normal effect towards the ultra-violet.

Pohl and Pringsheim also investigated alloys of potassium with other elements<sup>2</sup>. The alloys examined were those with Bi, Sb, and P, and those with Bi, Pb, Tl, and Hg. The first three belong to the same column of the periodic series and the other four to the same horizontal row. Only alloys with Tl and Hg showed any trace of a selective effect, the maxima being at  $\lambda$  3000 and  $\lambda$  3800 respectively. The long wave-length limit of the normal effect was more or less displaced in the case of the other alloys. The approximate limits for the Bi, Pb, Sb, and P alloys were  $\lambda$  4600,

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xii. p. 697, 1910.

<sup>2</sup> *Ibid.* xii. p. 1039, 1910.

$\lambda 4400$ ,  $\lambda 4000$  and  $\lambda 3600$  respectively. We may summarize these results by saying that the photo-electric effect of an alloy containing potassium differs more from the photo-electric effect of pure potassium, the more electro-negative is the other component.

Pohl and Pringsheim<sup>1</sup> found that there was no evidence of a selective photo-electric effect for Tl, Pb, Sn, Cd, and Bi, and of course one may infer the same conclusion for Sb and P mentioned above. Some interesting results were obtained for the normal effect. Since all the metallic surfaces were prepared in vacuo, the results for different metals are more comparable with each other than is usually the case. The results given in the paper are here put into different units in order to bring out the fact that the variation of the photo-electric effect from one wavelength to another is much the same for the metals which show no selective effect.

Wave-length	Photo-electric current per unit incident energy				
	Tl	Pb	Sn	Cd	Bi
3650	<1	<1	<1	0	0
3130	5·8	1·6	1·4	<1	<1
2540	62·1	50·4	55·2	59·2	56·3
2300	100	100	100	100	100

As may be seen, the differences of the effects for  $\lambda 2300$  and  $\lambda 2540$  are approximately the same for all metals and this also holds for  $\lambda 2540$  and  $\lambda 3130$ .

On investigating the photo-electric effect of calcium in the same way, results were obtained from which it might be concluded that calcium has a selective effect with a maximum near  $\lambda 3500$ <sup>2</sup>. Further experiments showed that this was not the case. As the angle of incidence of the light on the calcium surface was increased, the curves changed as shown in Fig. 22. We see that when the angle of incidence is  $70^\circ$ , the part which is like a selective effect has disappeared entirely. The real selective effect, on the other hand, as obtained with Na-K alloy, Fig. 20, becomes

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xiii. p. 474, 1911.

<sup>2</sup> *Ibid.* xv. p. 111, 1913.

more and more marked as the angle of incidence is increased. The authors explain the effect in calcium as being due to the greater penetrating powers of the shorter waves, and consequently fewer of the photo-electrons produced by the shorter waves emerge as compared with those produced by the longer waves. When the incidence is oblique, the absorption of light takes place in a thinner layer of the surface; and the electrons, whether

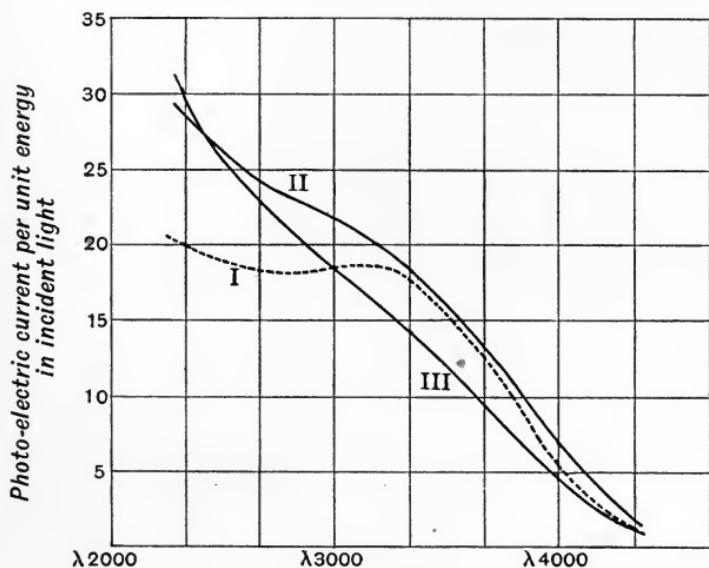


Fig. 22. Calcium.

Angle of incidence

I  $0^\circ$ ,

II  $45^\circ$ ,

III  $70^\circ$ .

produced by the light of longer or of shorter wave-lengths, have more equal chances of emerging. Thus a maximum in the curve does not of itself prove that a metal has a real selective effect. It is necessary either to show that it is produced only by light polarised in the  $E \parallel$  plane, or else that the effect becomes more marked with increasing incidence. Hence further experiments are required to decide whether the maxima obtained for Ba and for K-Hg alloys indicate real selective effects.

All the results above relate to the photo-electric effect in terms of the energy of the *incident* light. Lately Pohl and Pringsheim<sup>1</sup>

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xv. p. 173, 1913.

have, by an ingenious method, measured the photo-electric effect in terms of the energy *absorbed* from the beam of light. This is a great improvement and makes for precision in interpreting the results of the experiments. In Fig. 23 we have two curves, one giving the photo-electric effect for potassium per unit intensity of the incident light, and the other the photo-electric effect per unit intensity of the absorbed light. It is quite evident from the curves that the region in which the selective effect appears is a region of exceptionally high reflecting power.

The selective effect stands out still more clearly when the colloidal modifications of the alkali metals are investigated<sup>1</sup>. In

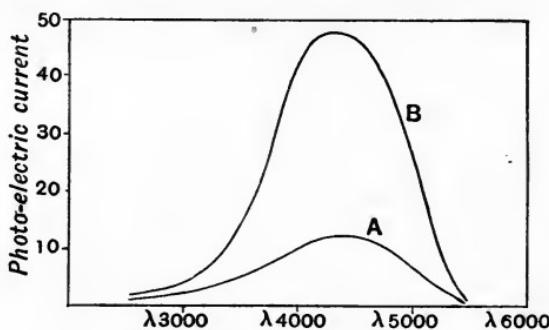


Fig. 23. Potassium.

A refers to incident light. B refers to absorbed light.

this case the total energy of the photo-electrons emitted in the selective region is as high as 2 % to 3 % of the energy in the absorbed light.

#### *Theoretical Considerations as to the Selective Effect.*

No satisfactory explanation of the selective effect is yet available. Pohl and Pringsheim have suggested that it is a molecular resonance phenomenon in which the electron follows the electric force, and thus the much greater number of electrons which emerge when the electric force has a component normal to the surface is accounted for. The form of the curve for the selective effect strongly suggests some kind of resonance. Presumably, on this view, all the systems concerned have the same period which }

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xv. p. 173, 1913.

corresponds to  $\lambda_{\max}$ . But the great width of the curve for the selective effect—about an octave—implies strong damping of the motion of the electron involved, far greater than occurs in the systems usually considered. If the systems concerned have a natural period corresponding to  $\lambda_{\max}$ , then we should expect rather more electrons to be emitted near this wave-length even when the light is polarised in the  $E \perp$  plane. For if the electrons are now ejected from their systems parallel to and in the surface, then a certain proportion may be scattered outwards, and we should expect more of these to emerge from the surface when illuminated by light of the wave-length  $\lambda_{\max}$  as more systems lose electrons under this condition. This is not the case. The difficulty can be avoided by assuming, as Lindemann<sup>1</sup> has done, that the systems concerned only allow the electron to vibrate normally to the surface. This seems rather an artificial conception, and moreover it has been pointed out before that the energy of an electron ejected from a linear system should depend on the intensity of the light.

A knowledge both of the distribution of velocities amongst the electrons emitted in the selective effect and also of their directions of emergence would be necessary for proper discussion of this question. It seems fairly evident, however, from Elster and Geitel's experiment (p. 78) that the velocities of the photo-electrons are much the same whether they are emitted in the selective or in the normal effects. It seems likely therefore that both sets of electrons originate in the same kind of system and therefore the introduction of a special kind of resonant system to account for the selective effect is unnecessary. To account then for the much greater number of electrons emitted with light of certain wave-lengths polarised in the  $E \parallel$  plane, it seems necessary to attribute the effect to some singularity in the optical properties of the surface. Very little is known about the optical properties of the alkali metals, the only investigations giving the optical constants of sodium and potassium being those of Duncan<sup>2</sup> which unfortunately do not extend as far as  $\lambda_{\max}$  for these metals. But Pohl and Pringsheim have made the important observation that

<sup>1</sup> Lindemann, *Verh. d. Deutsch. Phys. Ges.* XIII. p. 482, 1911.

<sup>2</sup> Duncan, *Phys. Rev.* (2) I. p. 294, 1913.

the selective region is also a region of high reflecting power. Consequently, according to optical theory, the part of the light which goes into the surface is very quickly absorbed, and the photo-electrons corresponding to this region have a much greater chance of emerging as they are released nearer the surface than the others. It would be interesting to see whether the high reflecting power of the surface in this region is confined to light polarised in the  $E \parallel$  plane, or whether it is shared by light polarised in the  $E \perp$  plane as well. It should be mentioned that the ordinary optical theory of metals does not indicate that the rate of absorption of light should depend on the state of polarisation. But Quincke<sup>1</sup> has shown that the penetrating power of the light depends, to some extent, on its plane of polarisation. The possibility that the selective effect is in some way related to the optical properties of the surface is perhaps not wholly without foundation. The wave-length at which the selective effect is a maximum does not seem to be connected with any of the known optical properties of the metals. All that we can say is, that the selective maxima shift towards the red as we pass from Li to Cs and a similar relation holds for the "convergence frequency" of the principal spectral series for the same metals.

To identify, as we have suggested, the selective and normal effects as fundamentally the same process is, perhaps, simplifying the conception of the photo-electric effect at the expense of the optical theory. But little is known about the optical properties of the alkali metals and the experimental result that the velocities of the photo-electrons are of the same order, whether produced in the selective or in the normal effect, is a very strong argument in favour of regarding the effects, from the photo-electric point of view, as fundamentally identical.

#### *Sensitiveness of Aluminium, Magnesium and Calcium.*

Pohl and Pringsheim described some remarkable experiments on the photo-electric effects of distilled aluminium, magnesium and calcium in which there was a great change of sensitiveness within

<sup>1</sup> Quincke, *Pogg. Ann. cxxix.* p. 177, 1866.

a few hours after the surface had been formed<sup>1</sup>. The metals were distilled in a very good vacuum and the photo-electric sensitiveness of the distilled portion was measured at intervals. Some curves for magnesium are produced in Fig. 24 and they are typical of the curves for the other two metals. The sensitiveness increases very appreciably in the course of a day and after a time a maximum appears in the curves. A still more remarkable effect is the growth of sensitiveness in the visible part of the spectrum and even in the infra-red. These results are difficult to reconcile with those of Richardson

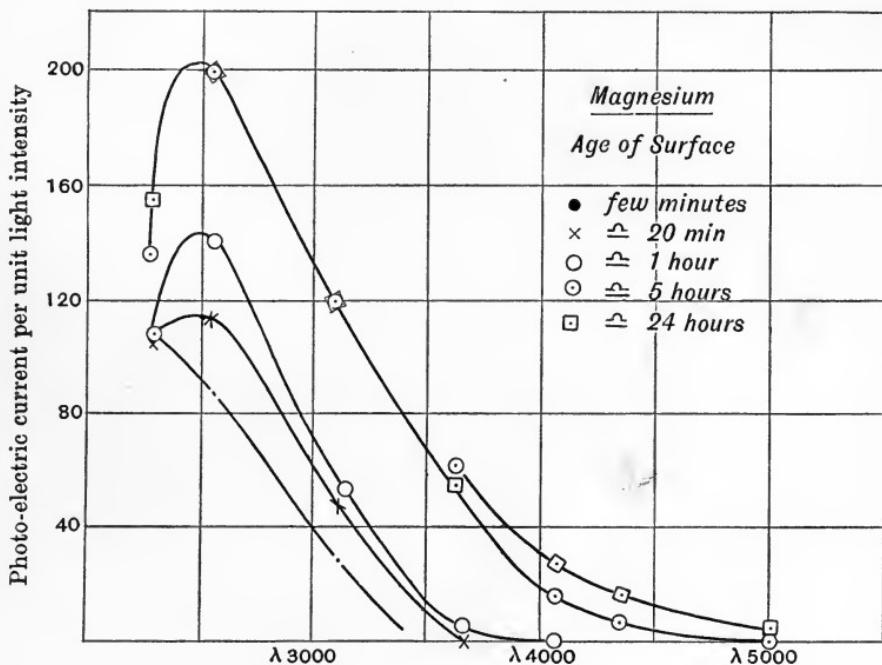


Fig. 24.

and Compton and the writer. Applying the formula  $V = kn - V_0$  to these results indicates that, if the photo-electric effect extends to  $\lambda 7000$ ,  $V_0$  has a value as small as 1·5 volts. If this interpretation is correct, one would expect these metals to emit thermionic currents at quite low temperatures. The appearance of a maximum on the curve does not indicate the presence of a selective effect. In the case of calcium, it was shown that the maximum disappeared at oblique incidences and one may presume the same to be the case for

<sup>1</sup> Pohl and Pringsheim, *Verh. d. Deutsch. Phys. Ges.* xiv. p. 546, 1912; xv. p. 111, 1913.

magnesium and for aluminium. One may possibly explain the change in sensitiveness in this way. Immediately after distillation, the surface layers are, like the interior, amorphous in structure, but after a time a definite structure is formed in the surface. The change from the amorphous state to the more permanent state will very likely be accompanied by changes in the absorbing power of the substance both for electrons and for light. It is also possible that some re-adjustment of the occluded gases in the recently formed surface layers takes place and that the change of sensitiveness with the time is associated with this. This of course does not explain why the sensitiveness to the red and infra-red makes its appearance.

*Infinite + Contradictory*

CHAPTER VI

PHOTO-ELECTRIC PROPERTIES OF THIN METALLIC FILMS

RÖNTGEN rays and  $\gamma$ -rays on passing through thin films are known to produce different ionisation effects on the two sides. The number of electrons and of secondary rays is greater on the side from which the main beam emerges. On the other hand, the velocities of the electrons emitted on both sides of a thin sheet of metal struck by X-rays appear to be the same (Beatty<sup>1</sup>). Similar asymmetric effects have been observed with the photo-electrons emitted on the two sides of a thin film. From general considerations, one might expect rather more electrons to emerge in the direction in which the light is travelling, on account of the momentum which the light imparts to the electrons in that direction. Closer investigation however shows that the momentum imparted is much too small to account for the effects observed. We shall refer to the side of a thin film on which the light falls as the *incident* side, and to the other side as the *emergent* side. There are two distinct effects to be investigated, the asymmetry in the number of the photo-electrons emitted on the two sides, and the asymmetry in their velocities. Of the two, the latter is perhaps the more difficult to investigate successfully.

The films necessary for these experiments have to be so thin (semi-transparent) that they must be supported in some way. They are produced by placing a quartz plate below the cathode in a discharge tube and passing the discharge until a layer of the metal of suitable thickness is sputtered on to the plate from the cathode.

<sup>1</sup> Beatty, *Phil. Mag.* xx. p. 320, 1910.

*Asymmetry in the Numbers of Photo-Electrons emitted from the two Sides of a thin Film.*

Kleeman<sup>1</sup> found that the ionisation produced in air was 15 % greater on the emergent side of a thin platinum film than on the incident side. If the photo-electrons emitted on both sides have the same distribution of velocities, then the ionisation produced is proportional to the number of electrons emitted. Kleeman also found that 17 % more electrons were emitted on the emergent side of the platinum film in vacuo than on the incident side.

Stuhlmann<sup>2</sup> measured the photo-electric effect on the two sides of a platinum film in air and found 17 % excess on the emergent side. The following table contains the results of similar experiments on other metals.

Period	Metal	Ratio emergent effect incident effect	Ratio Atomic Weight $\times 10^4$
II	Mg	1.06	435
III	Fe	1.02	182
IV	Cu	1.08	170
	Zn	1.11	170
VI	Ag	1.07	99
	Sn	1.15	97
VII	Pt	1.17	60
IX	Pb	1.12	54

Stuhlmann pointed out that the ratio of the emergent to the incident effect, divided by the atomic weight, is constant for elements of the same period (or row) in the periodic table. The quotient decreases consistently as we pass from one period to the next. No explanation for this law is suggested. It is unfortunate that the number of elements which can be tested for this effect is restricted on account of the great difficulty of sputtering uniform layers of most of the other elements.

<sup>1</sup> Kleeman, *Proc. Roy. Soc. A.* LXXXIV. p. 92, 1910.

<sup>2</sup> Stuhlmann, *Phil. Mag.* xx. p. 331, 1910; xxii. p. 854, 1911.

From the recent work of Partzsch and Hallwachs<sup>1</sup>, it now seems very doubtful whether the above-mentioned results imply any asymmetry at all in the photo-electric effect on the two sides of a thin film. The asymmetry seems to arise from the different amounts of light absorbed by the film, according as the light enters from the air side, or from the quartz side. If  $E_q$  is the amount of light penetrating the film when the light is incident on the quartz side, and  $E_a$  the amount when the light comes from the air side, then

$$\frac{E_q}{E_a} = n_q \frac{1 + n^2(1 + k^2) + 2n}{n_q^2 + n^2(1 + k^2) + 2nn_q},$$

where  $n_q$  is the refractive index of quartz, and  $n$  and  $k$  the optical constants for the metal forming the film. This ratio, calculated for  $\lambda 2570$ , is for the following metals:

Fe	Ag	Cu	Pt
1.015	1.125	1.13	1.14

Stuhlmann's values for the asymmetry in the photo-electric effect are:

Fe	Ag	Cu	Pt
1.02	1.07	1.08	1.17

It seems that here we have the clue to the explanation of the asymmetry, viz. that it depends on the different amounts of light absorbed, according to the direction of the incident light. The formula above does not take into account multiple reflections. The authors then investigated by direct experiment the absorption of light by platinum films on quartz. They found that when a beam of light was incident from the quartz side 40% more light was absorbed in the film than when the beam was incident on the air side of the film. In view of this ratio, it cannot be maintained that it has been shown that any asymmetry exists in the number of photo-electrons emitted from a thin film when equal amounts of light are absorbed.

Partzsch and Hallwachs conclude that 99% of the photo-electrons emerge from a layer thinner than  $28 \times 10^{-7}$  cm. and that only 1% of the light penetrates beyond  $78 \times 10^{-7}$  cm. It would be very desirable to investigate this matter again with light of different wave-lengths. It is probable that the penetrating power of the photo-electrons would increase with their velocity.

<sup>1</sup> Partzsch and Hallwachs, *Ann. d. Phys.* xli. p. 247, 1913.

*Asymmetry in the Velocities of Photo-Electrons emitted from the two Sides of a thin Film.*

The velocities of the photo-electrons emitted by a thin platinum film on the incident and on the emergent side have been investigated by Robinson<sup>1</sup> simultaneously with the numbers. In Fig. 25 the curve *A* represents the variation in the ratio of the numbers emitted on the two sides, and curve *B* the variation in the ratio of the maximum emission energies, with the thickness of the film. The results as to the ratio of the numbers of the photo-electrons are open to criticism on the grounds of Partzsch and Hallwachs' experiments. But the criticism does not apply to the ratio of the *velocities*. Continuing curve *B* backwards we get an estimate of the ratio which would correspond to a very thin film from which

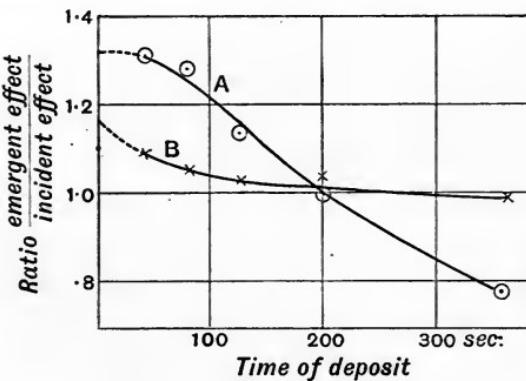


Fig. 25.

Thickness of film assumed to be proportional to time of deposit.

disturbing influences are absent. This limiting ratio for the maximum emission energies comes out as 1·12. The excess of energy on the emergent side suggests that the electrons are originally ejected from the molecules in the direction of the light, and that a loss of energy occurs when they swing round so as to emerge on the incident side. In the experiments recorded on pp. 40 and 41 it will be noticed that the energy of the photo-electrons deviates from that predicted by the quantum theory by about 10% to 25% according to the nature of the metal. For platinum, the deviation is 14%. But this is practically identical with the difference

<sup>1</sup> Robinson, *Phil. Mag.* xxv. p. 115, 1913.

between the emission energies on the emergent and on the incident sides. Hence we should expect a good agreement between the quantum theory and experiments if we considered the electrons which emerge *with* the light. The quantum theory does not of course explain the nature of the process, it only deals with energies transferred. Should this view be the correct one, viz. that the quantum theory accounts for the energies of the photo-electrons in a quantitative manner, it affords still another example of the occurrence of the constant  $h$  in physics.

The experimental evidence on this point is very meagre and not altogether convincing, and much more is wanted to test the view advanced. Since the energies of the photo-electrons depend only on the wave-length, it is not clear why the ratio (curve *B*) decreases with increasing thickness, unless perhaps the shorter waves are gradually cut out by the increasing thickness. From optical theory, however, one would expect the shorter waves to penetrate deeper than the longer waves.

### *The Electro-magnetic Theory and Asymmetry.*

The electro-magnetic theory of light does not indicate any asymmetry of a measurable order in the photo-electric effect. Richardson's treatment<sup>1</sup> is as follows. If  $E$  is the energy imparted by light to an absorbing system, then, on the electro-magnetic theory, the momentum imparted is  $E/c$ , where  $c$  is the velocity of light. Now consider an electron absorbing  $hn$  units of energy. It will also absorb  $hn/c$  units of momentum. Then the mean kinetic energy of the electrons will be

$$\frac{1}{2}mv^2 = hn,$$

where  $v^2$  is the mean square of the velocities. The average momentum in the onward direction will be

$$m\bar{u} = \frac{hn}{c},$$

where  $\bar{u}$  is the average component of the velocity in the onward direction. Hence

$$\frac{\bar{u}}{v} = \frac{v}{2c}.$$

<sup>1</sup> Richardson, *Phil. Mag.* xxv. p. 144, 1913.

$$v^2 = \frac{2hn}{m}$$

$\left\{ \quad \right.$

$$v^2 = 2mc$$

For electrons whose velocity is  $6 \times 10^9$  cm./sec., this yields an asymmetry of  $\frac{1}{10}$ , which is of the order of the asymmetry in the ionisation on either side of a thin sheet struck by Röntgen rays. But for photo-electrons, whose velocity is about  $6 \times 10^7$  cm./sec., the ratio  $\bar{u}/v$  is only  $\frac{1}{1000}$  and therefore we should not expect any measurable asymmetry.

Swann<sup>1</sup> investigated the direct effect of the electric and magnetic forces in a beam of light on a free electron and arrived at the same result as Richardson for the component of velocity in the onward direction. Thus the classical electro-magnetic theory leads to a measurable asymmetry for the ionisation by Röntgen rays, but not for photo-electric effects.

It is assumed in the foregoing discussion that a photo-electron acquires its energy from the light. We have seen before that it is not easy to reconcile this view with the conception of a continuous wave front. To explain the photo-electric effect, while retaining the conception of a continuous wave front, it seems necessary to introduce some kind of a resonance system in which light produces instability and causes the electron to be emitted with the energy it had in its orbit. The investigation of a resonance system of this kind for asymmetric emission when acted on by the forces in a light wave has not been done and would probably be difficult.

### *Peculiarities in the Photo-Electric Properties of thin Films.*

Dike<sup>2</sup> investigated the way in which the velocities of photo-electrons (on the incident side only) from thin platinum films varied with the thickness. Extraordinarily high velocities were obtained, the greatest corresponding to about 50 volts. Values exceeding 15 or 20 volts were very frequently obtained. The velocities were highest when the thickness of the film was between  $10^{-8}$  and  $10^{-7}$  cm.; thicker films gave, on the whole, smaller velocities, though still big compared with velocities usually obtained. Dike and Brown<sup>3</sup> confirmed these results, but do not now seem quite convinced that the experiments indicate that the photo-electrons have

<sup>1</sup> Swann, *Phil. Mag.* xxv. p. 534, 1913.

<sup>2</sup> Dike, *Phys. Rev.* xxxiv. p. 459, 1912.

<sup>3</sup> Dike and Brown, *Phys. Rev.* (2) i. p. 254, 1913.

really these high velocities. No details as to the effective wavelengths in Dike's experiments are given, but it appears that ultra-violet light was necessary. The photo-electrons from thin films in Robinson's experiments<sup>1</sup> did not possess exceptional velocities.

Emission velocities corresponding to values as high as 10 volts are quite incapable of interpretation on the quantum theory. Values less than the theoretical value can be accounted for in various ways, but values in excess cannot be explained away. It seems very probable that the abnormal velocities are due to the abnormal contact potential differences between the illuminated surface and the surrounding electrode. Very considerable surface polarisation at the electrodes exists when a discharge has recently

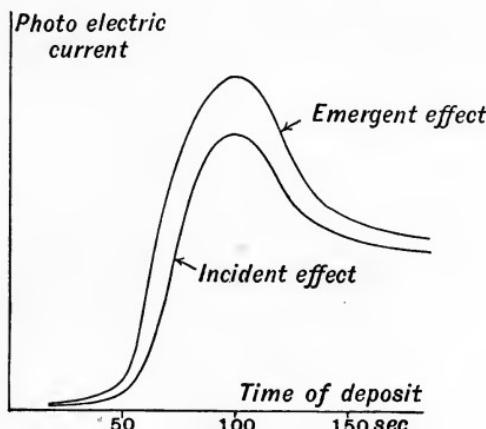


Fig. 26.

Thickness of film assumed to be proportional to time of deposit.

100 sec. corresponds to  $10^{-7}$  cm.

passed through the apparatus (von Baeyer and Tool). It is very probable that if the contact potential were measured at the same time as the velocity experiments were made, the high velocities would be accounted for.

Robinson<sup>1</sup> found that the photo-electric current from a thin platinum film increased very rapidly with the thickness up to  $10^{-7}$  cm., and then fell off again (Fig. 26). As the thickness of the film increases, more light is absorbed and consequently one would

<sup>1</sup> Robinson, *Phil. Mag.* xxv. p. 115, 1913.

expect the photo-electric effect to increase with the thickness though hardly so rapidly as it does. But we must bear in mind that very thin metallic films may perhaps absorb less light than that calculated by the ordinary exponential law of absorption and thus a more rapid increase might be accounted for. The meaning of the term "thickness of film" becomes rather indefinite when we deal with distances of the order of a few molecular diameters. It was at a thickness of about  $10^{-7}$  cm. that Patterson found that the electrical resistance of a film began to deviate from the calculated values.

## CHAPTER VII

### PHOTO-ELECTRIC EFFECTS OF NON-METALLIC ELEMENTS AND INORGANIC COMPOUNDS

WE have seen that the photo-electric effect for metals sets in at a definite wave-length characteristic of the metal. The formula giving the relation between the maximum emission energies and the frequency

$$V = kn - V_0$$

indicates that there is no photo-electric effect with frequencies less than  $n_0 = V_0/k$ , or with wave-lengths longer than  $\lambda_0 = c/n_0$ .  $V_0e$  is the work expended in escaping from the parent molecule, and this is least for the electro-positive metals. Though we have but few experiments on the velocities with which photo-electrons escape from compounds, yet analogy, and the experiments we have, lead us to assume that the same law holds for compounds as for metals. We can therefore calculate from the long wave-length limit the work required for an electron to escape from its parent molecule whatever this may be.

Sir J. J. Thomson has introduced the conception of corpuscular pressure in molecules (*Corpuscular Theory of Matter*, p. 119). In metals such as sodium, the corpuscular pressure is high and an electron is easily detached. When the corpuscular pressure is low as in chlorine, which has a great avidity for electrons, much more work is required to detach an electron. Photo-electrons are easily obtained from sodium with visible light, but even the shortest wave-lengths available fail to ionise chlorine. When two elements combine, we may consider an equalization of the corpuscular pressures to take place. The difference in the corpuscular pressures is indicated by the heat of formation which is great or small as the

corpuscular pressures of the combining elements differ much or little. When an electro-positive substance like sodium combines with oxygen, a great reduction in the corpuscular pressure takes place, and, corresponding to this, the long wave-length limit of the photo-electric effect is removed far into the ultra-violet. On the other hand, little heat is developed when a halogen combines with silver, and the photo-electric effects in the metal and in the compound are of the same order. Another illustration is the small effect in the oxides of the metals compared with the effect in the sulphides which are sometimes of the same order of activity as the metals themselves. The heats of formation of the oxides are generally considerably greater than those of the sulphides. Also the effect for oxygen starts at  $\lambda 1350$ , while sulphur is sensitive to the light from a mercury lamp. With the evidence at present available, one can only conclude that this view is, in general, qualitatively correct. The departures from quantitative agreement are more marked when we compare compounds of different types. It is evident that in comparing compounds containing elements of different valencies, the valency has, in some way, to be taken into consideration in addition to the heat of formation.

When we collect the experimental results, we find that in almost all experiments the only thing measured is the total photo-electric effect and that the light is usually unresolved. Information as to the velocities of the photo-electrons and as to the active spectral region is generally wanting. As a rule, light penetrates deeper into compounds than into metals; hence if photo-electrons of the same number and velocity are produced in both cases, fewer emerge from the compounds than from the metals. This is important, and should be borne in mind when comparing photo-electric effects. As an approximation, however, we may conclude that the greater the total photo-electric effect is, the nearer to the visible is the long wave-length limit of the active spectral region. The accuracy of this conclusion depends upon the considerations mentioned above of the rapidity with which the light is absorbed.

A large number of the substances to be mentioned are more or less insulators and this has to be met by special experimental arrangements. When the material is laid on a metal tray in thin layers, quite a small conductivity will suffice to keep the illuminated

surface at the same potential as the tray. But if the material insulates, the surface will charge up positively as the photo-electrons stream away, until the potential is high enough to prevent the escape of more. This gives a quasi-fatigue effect, but the term fatigue in this connection should be avoided as it leads to confusion with the phenomenon observed in metals. One way in which the accumulated charge has been measured is to transfer the charged material into a Faraday cylinder connected to an electrometer. The deflection of the electrometer is proportional to the charge on the material inside the Faraday cylinder. If the material is only a fair insulator, then time will enable the charge to dissipate away so as to leave the material at zero potential. If however the material is a very good insulator, this process takes too long and it is necessary to start with fresh material for each experiment.

### *Elements.*

The gaseous elements whose photo-electric effects have been investigated are dealt with in the chapter on ionisation in gases. Only a few of the other non-metallic elements have been examined photo-electrically.

The author<sup>1</sup> found that arsenic and selenium gave off photo-electrons when illuminated by the light from a mercury lamp. The same law between the velocity and the frequency held for these two elements as for the metals. The longest wave-length which was effective in exciting the emission of photo-electrons was  $\lambda 2360$  for arsenic and  $\lambda 2200$  for selenium. The author found that carbon in the form of soot deposited on a cold plate from a xylol flame was sensitive photo-electrically as far as  $\lambda 2550$  or  $\lambda 2600$ .

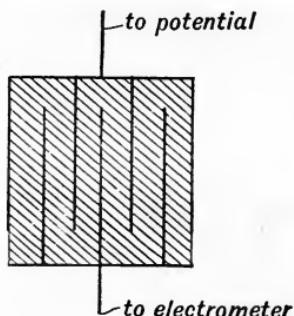
The photo-electric effect of sulphur has been investigated in great detail by Goldmann and Kalandyk<sup>2</sup>. Some peculiarities in the behaviour of illuminated sulphur are shared by other insulators and it is desirable to describe the experiments at some length. When light is absorbed by a photo-electrically active substance in a layer of appreciable thickness, one would expect photo-electrons to be released in the substance itself as well as from the surface.

<sup>1</sup> Hughes, *Phil. Trans. A.* ccxii. p. 205, 1912.

<sup>2</sup> Goldmann and Kalandyk, *Ann. d. Phys.* xxxvi. p. 589, 1911.

If the substance is not naturally a good conductor, then the photo-electrons which do not emerge should impart a slight conductivity during illumination. In other words, the substance has temporarily a number of free electrons and these account for the conductivity. That such is the case is supported by the experiments of Goldmann and Kalandyk on sulphur and by other experiments on insulators.

For investigating the conductivity effect due to illumination apart from the photo-electric effect at the surface, the authors used the arrangement shown in Fig. 27. It is essentially a piece of sulphur between two electrodes. When illuminated by a mercury



The shaded portion represents sulphur.  
The light was incident vertically downwards (at right angles to the plane of the paper).

Fig. 27.

lamp, the sulphur acquired a conductivity which was independent of the applied field up to 400 volts per mm. (Higher voltages were not tried. It would be interesting to see whether saturation

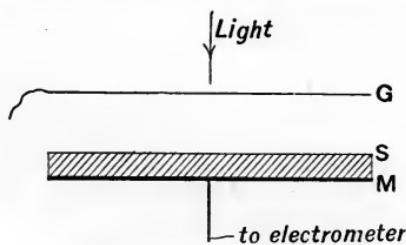


Fig. 28.

could be obtained with higher fields.) The order of the current passing through the illuminated sulphur was  $2 \times 10^{-9}$  amp. with this field.

In the second form of apparatus used, the sulphur *S*, or other dielectric, is placed on a metal plate *M*, Fig. 28. A gauze *G* which can be maintained at any required potential is arranged parallel

to the surface of  $S$ . When  $G$  is at a negative potential, the electrometer will acquire a negative charge due to (a) the emission of photo-electrons from  $G$  to  $S$ , (b) the conductivity produced in the thin illuminated layer of sulphur. If the illuminated layer does not reach down to  $M$ , then a separation of charges takes place in the thin layer of sulphur until the external field in it is annulled. This may be regarded as a polarisation of the dielectric which is shown by the electrometer acquiring a negative charge that after a time becomes constant. This is the case shown in curve III, Fig. 29. If the illuminated layer reaches down to the metal plate

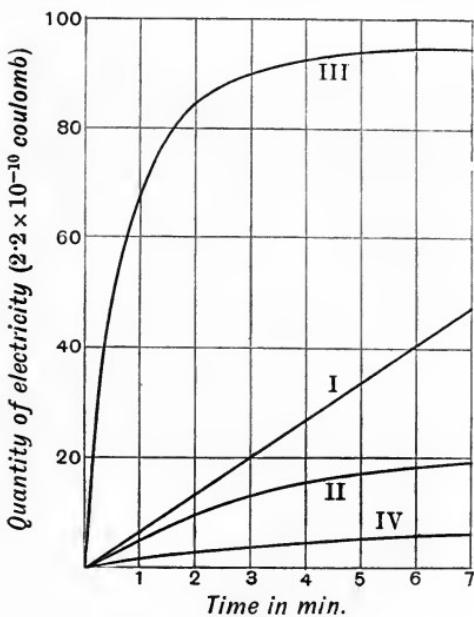


Fig. 29.

- I = 1 mm. air.
- II = 1 mm. air + 1 mm. paraffin.
- III = 1 mm. air + 1 mm. sulphur.
- IV = 1 mm. paraffin.

$M$ , then the sulphur does not insulate and a final charge is not obtained. A steady state is reached, after initial polarisation effects, when a constant leak occurs and this is a measure of the photo-electric current from the gauze to the sulphur, which as a temporary conductor affords passage for the electricity.

When  $G$  is at a positive potential, the electrometer system acquires a positive charge due to (a) the escape of photo-electrons

(if any) from the surface of the sulphur to the gauze, and (b) the conductivity induced in the sulphur leading to a final polarisation when the layer is thick. If the layer is so thin that the sulphur conducts throughout, then the steady current obtained is a measure of the photo-electric effect from the surface.

In Fig. 30 we have curves for the case of a sulphur layer 2 mm. thick and an air gap of 3 mm. Since the ordinates of curve II are greater than those of curve I, we see that the polarisation effect + photo-electric leak from the sulphur is greater than the polarisation effect + leak from the gauze. The polarisation effect is independent of the direction of the field. The surface effect appears

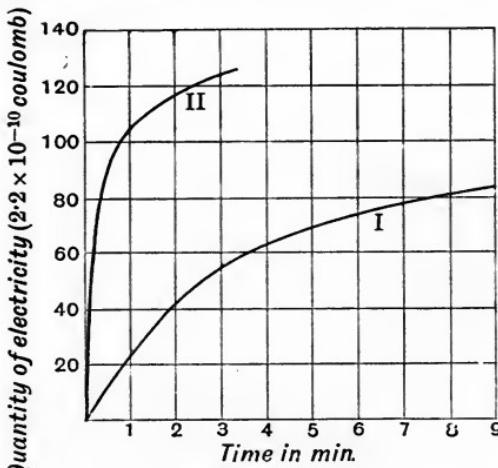


Fig. 30.

I = Gauze at negative potential.

II = Gauze at positive potential.

to be quite big in comparison with the polarisation effect, but we must be careful about drawing conclusions from this as to the relative number of electrons involved in both processes. The transport of an electron from the sulphur surface to the gauze produces a much bigger effect than the transport of an electron through the very thin layer of illuminated sulphur. (The electron involved in the polarisation effect only moves a short distance, and thus the induced charge produced in  $M$  by this movement is much less than the loss of charge by  $M$  when an electron is actually transferred from  $G$  to  $M$ .) Hence the method exaggerates the effect due to surface photo-electric effect over that due to the

induced conductivity. Probably the electrons which are released in the sulphur and so cause the conductivity do not emerge from the surface when they get there as their velocity has been reduced to that of a free electron by repeated collisions. Those which emerge are released from the surface molecules with the necessary emission velocities.

The effect of thickness is well shown in Fig. 31. When the illuminated layer reaches down to the metallic backing, then a steady leak is obtained. When the illuminated layer does not reach through the sulphur, then the leak ceases after a time and

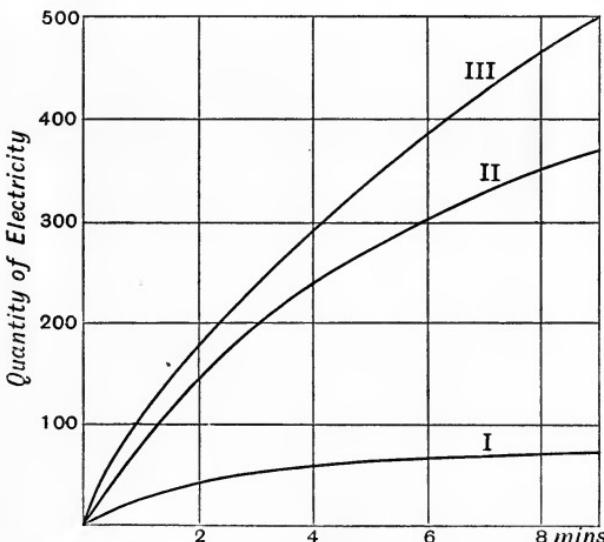


Fig. 31.

- I. Thickness of sulphur = 1 mm.
- II. " " " = .5 mm.
- III. " " " = .2—3 mm.

the sulphur has reached its final state of polarisation. The curves show that the effective depth of penetration is about 3 mm.

It is difficult to determine the ratio of the number of electrons emitted from the surface to the number released in the illuminated layer. It is very probable that the latter predominates. It has already been indicated that the experiments give less weight to the latter effect. Again, in the transverse effect (i.e. the effect investigated by the arrangement shown in Fig. 27), no approach to saturation was observed and hence the number of electrons set

free per second by the light must be much greater than is given by the current divided by the charge on an electron. We may therefore be justified in considering that more electrons are released by the light *in* the illuminated layer than are emitted *from* the surface. From analogy with other substances, mentioned below, it is probable that the surface effect requires light of shorter wave-lengths to produce it than the conductivity effect requires. Experiments on this point would have been useful. Goldmann and Kalandyk mention that the whole effect is cut off by a glass plate which probably means that the effect requires light of wave-lengths shorter than  $\lambda 3300$  to produce it.

It is well known that selenium becomes a conductor when illuminated by visible light, yet its photo-electric effect only sets in at  $\lambda 2200$ . There seems little doubt that the change in conductivity, or part of it, arises from electrons which are set free (Ries<sup>1</sup>). It should be mentioned that some experimenters believe that an allotropic modification of selenium is formed by the light and that there is an equilibrium between this and the form which is stable in the dark. The modification has the property of conducting electricity. The results of experiments on the conductivity of selenium appear to be more complicated than those on sulphur, and it is possible that the phenomena cannot be accounted for adequately by the setting free of electrons and that some photo-chemical change takes place in addition. However, it seems well-established that the escape of photo-electrons from the surface of many non-metallic substances requires light of shorter wavelength than is necessary to produce the increased conductivity. In other words, the long wave-length limit of the conductivity effect is further towards the red than that of the photo-electric effect. This view is supported by Wilson's experiments on silver iodide, Volmer's experiments on anthracene, Pauli's experiments on the relation between fluorescence and the photo-electric effect, and the experiments of Lenard and Saeland on phosphorescent substances, and experiments on selenium. It is very probable that sulphur behaves in a like manner, though Goldmann and Kalandyk did not make any experiments bearing directly on this point.

<sup>1</sup> Ries, *Phys. Zeits.* XII. p. 530, 1911.

In experiments, arranged as in the experiment on sulphur, Fig. 28, the change of conductivity in the illuminated sheet of an insulator can only produce a polarisation effect, when the temporarily conducting sheet is not in contact with the metal electrodes. The electrometer does not, as in most photo-electric experiments, acquire a charge at a constant rate, but the rate of charging decreases to zero, indicating that the final state of polarisation has been reached. This process has been called the actino-dielectric effect to distinguish it from the photo-electric effect.

In the formula

$$V = kn - V_0,$$

representing the relation between the potential corresponding to the maximum emission velocity and the frequency, we have regarded  $V_0e$  as the energy spent by an electron in getting away from the surface molecules. If now less energy is required to separate an electron from a molecule inside a solid or liquid than to remove an electron from a surface molecule into the surrounding medium, we should expect the increased conductivity to be produced by light of longer wave-length than is necessary to produce the photo-electric effect. On this view,  $V_0$  for a molecule of sulphur surrounded on all sides by other similar molecules would be less than for the molecules forming the surface layer. The experimental results for a number of substances are in agreement with this view.

Though several attempts to obtain ionisation of iodine vapour when illuminated by ultra-violet light have been made, no investigations of the photo-electric effect in solid iodine appear to be on record.

There is one very important problem in photo-electricity on which it is very desirable to have information. How does the number of electrons released, when unit energy of light is absorbed, vary with the frequency of the light? This information should be given by measuring the saturation currents through sulphur, or some other insulator, when illuminated by light of different wave-lengths. The results would be useful to compare with similar experiments on gases or vapours.

### Oxides.

There has been no systematic examination of the photo-electric properties of oxides. The effect for oxides and for most other compounds is frequently given in terms of the effect for some metal, and as the state of this metal is not usually specified, it is useless to attach any quantitative importance to the numbers, though they are useful as indicating the order of the effect.

Hallwachs<sup>1</sup> found that the effect for CuO and Cu<sub>2</sub>O was of the same order as that for Cu. Similar remarks apply to Pb and PbO<sub>2</sub>. W. Wilson<sup>2</sup> found that PbO<sub>2</sub> had a photo-electric effect which was about equal to that of Al and one quarter of that of Ag. A carbon arc was used by both. The author<sup>3</sup> found that CuO gave a marked photo-electric effect, which was about one hundredth of the effect for distilled metals like Pb, Zn, etc. (It should be remembered that these distilled metals give much bigger effects than metals which have been exposed to air.) It will be noticed that all the oxides mentioned are good conductors of electricity.

The author (*l.c.*) found that there was not a trace of a photo-electric emission from P<sub>2</sub>O<sub>5</sub> illuminated by a mercury lamp. BaO illuminated in the same way gave a very small effect, and as the substance was not pure it is possible that the small effect was due to the impurities. Both these oxides are insulators. They possess bigger heats of formation than the other oxides which show big photo-electric effects. Hence the results which are available on oxides support the view put forward at the beginning of the chapter.

### Sulphides.

According to Goldmann and Kalandyk's experiments, one may conclude that sulphur is certainly photo-electric with wave-lengths longer than  $\lambda 2000$ . Hence one would expect the photo-electric effect of a sulphide to set in between this limit and that of the metal. Also if the combination is not a vigorous one, the long wave-length limit of the metal should not be displaced much.

<sup>1</sup> Hallwachs, *Comptes Rendus Congrès Radiologie*, p. 2, 1910.

<sup>2</sup> W. Wilson, *Ann. d. Phys.* xxiii. p. 107, 1907.

<sup>3</sup> Hughes, *Phil. Mag.* xxiv. p. 308, 1912.

Experiments on this point have not been made, but, if the total photo-electric effect of a sulphide is of the same order as that of the metal, we may conclude that the long wave-length limits of both are approximately the same. We may also assume that the greater the difference between the total photo-electric effects, the greater is the separation between the corresponding long wave-length limits.

The most systematic experiments on the sulphides are those of Rohde<sup>1</sup>. He found that the photo-electric current from a sulphide depended very largely on its compactness. Chemically prepared sulphides were much less active than the minerals. If however they were compressed into a pastille under a pressure of 8000 atmospheres, they gave much the same effect as the corresponding mineral sulphides. The light used was from a zinc spark.

The following table gives the photo-electric currents from various sulphides together with the currents from aluminium and zinc under similar conditions:

		PbS	887	Fe <sub>7</sub> S <sub>8</sub>	122
		Cu <sub>2</sub> S	534	NiS	102
		CuS	391	CoAsS	89
Zn	530	MnS	355	ZnS*	80
Al	200	Ag <sub>2</sub> S	240	FeS	64
		Sns	236	CdS	58
		FeS <sub>2</sub>	176	Sb <sub>2</sub> S <sub>5</sub>	45
		Cr <sub>2</sub> S <sub>3</sub>	160	CoS	29
		MnS <sub>2</sub>	141	MoS	28
		Bi <sub>2</sub> S <sub>3</sub>	138		

The sensitiveness is of the same order as that of the metals and in some cases actually greater. However we must remember that the metals zinc and aluminium were not in the most active state. Before drawing the conclusion that the sulphide may be more active than the metal, the effect of the metal distilled in vacuo should be measured and compared with that of the sulphide. The metal is more easily affected adversely by contact with the atmosphere than the sulphide and this may account for the sulphides appearing to have a bigger effect. The author found that the sensitiveness of cadmium distilled in vacuo was reduced to one fifth

<sup>1</sup> Rohde, *Ann. d. Phys.* xix. p. 935, 1906.

by contact for 15 minutes with dry oxygen at a pressure of 150 mm. Knoblauch<sup>1</sup>, and Ramsey and Spencer<sup>2</sup> have obtained big effects with a number of sulphides.

Herrmann's results<sup>3</sup> are in general agreement with those of Rohde. The tellurides and selenides of the metals, like the sulphides, give big effects.

W. Wilson (*l.c.*) found that AgS was from two to three times as active as silver. In both cases only ultra-violet rays were effective.

Schmidt<sup>4</sup> obtained either very little or no effect with CaS, Ba<sub>4</sub>S, and SrS, but very big effects with other sulphides in which the metals were not so strongly basic. The corresponding sulphates were not photo-electrically active at all, hence the addition of oxygen to the molecules shifts the long wave-length limit beyond the range of the light (spark) used.

### *Salts.*

The halogen salts of silver have been known to be photo-electric for some time. Pochettino<sup>5</sup> gives the copper halides in order of their photo-electric effect as CuI<sub>2</sub>, CuBr<sub>2</sub>, CuCl<sub>2</sub> and CuF<sub>2</sub>. It is rather significant that this is the order of increasing stability and the order of decreasing photo-electric effect. As an indication of the magnitude of the effect it may be mentioned that the effect for CuO is intermediate between that for CuCl<sub>2</sub> and CuF<sub>2</sub>.

Reboul<sup>6</sup> found that the photo-electric effect of copper bromide increased with continued illumination and this was accompanied by a decomposition of the salt. After a prolonged illumination the effect began to decrease again, probably owing to the fatigue of the copper.

The author<sup>7</sup> found that much more satisfactory and consistent results could be obtained when the salts investigated were distilled *in vacuo*. Only under such conditions could one be certain that

<sup>1</sup> Knoblauch, *Zeits. phys. chem.* xxix. p. 527, 1898.

<sup>2</sup> Ramsey and Spencer, *Phil. Mag.* xii. p. 397, 1906.

<sup>3</sup> Herrmann, *Dissertation*, Berlin, 1908.

<sup>4</sup> Schmidt, *Ann. d. Phys.* lxiv. p. 708, 1898.

<sup>5</sup> Pochettino, *Accad. Lincei, Atti*, xv. p. 355, 1906.

<sup>6</sup> Reboul, *Comptes Rendus*, cliv. p. 424, 1912.

<sup>7</sup> Hughes, *Phil. Mag.* xxiv. p. 380, 1912.

the surface layer was identical with the rest of the substance. This method restricted the range of the investigation to those salts which volatilized at or below a red heat. The apparatus used is shown in Fig. 11, p. 38, and the procedure was the same as in the experiment on distilled metals. The light was obtained from a mercury lamp. The following results for mercurous chloride are typical :

*Mercurous chloride.*

		Photo-electric current
	First 20 secs.	$<7 \times 10^{-15}$ amp.
First exposure after distillation	Next ,,	3·5 "
	Next ,,	5·7 "
Exposed 5 mins.		26·4 "
" 5 "		40·5 "
In dark 6 "		40·5 "
" 6 "		35·0 "
Exposed 4		53·7 "
" 6 "		70·4 "

Hence mercurous chloride is *not* photo-electrically active in the first few seconds during which it is exposed to the light. The photo-electric current increases rapidly with the exposure but is checked by shutting off the light. At the end of the experiment, it was found that the distilled salt, originally white, had a grey metallic lustre on the exposed part. There is no doubt that the explanation is that the light, first of all, decomposes the salt, and then produces a photo-electric effect in the metallic mercury. Thus the effect of the light in this case is primarily photo-chemical. A similar effect was obtained with  $\text{HgCl}_2$ ,  $\text{HgI}$ ,  $\text{HgI}_2$  and  $\text{BiCl}_3$  and a very much smaller one with  $\text{PbI}_2$ . In the case of the iodides of mercury, the initial leak was not zero, but quite small. Probably the decomposition started too rapidly to enable the initial zero effect to be detected. There was not a trace of a photo-electric emission from  $\text{ZnCl}_2$  even after prolonged exposure. Under similar conditions, there was only the slightest indication of a photo-electric effect in  $\text{FeCl}_3$ . No discolouration was produced in these salts by prolonged illumination. The decomposition, and subsequent photo-electric effect, which is very feeble, or even non-existent, in  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ , and  $\text{PbI}_2$  is well marked in the mercury chlorides and iodides and in bismuth chloride. The first three are much more stable salts than the others.

Schmidt (*l.c.*) found that the stable salts NaCl, NaBr, NaI and NaF were not photo-electric with the light from a spark, while big effects were obtained with AgCl, AgBr and AgI. The effects for the latter were practically identical. A large number of sulphates and other salts, usually regarded as the more stable salts, gave no photo-electric effect.

The photo-electric experiments on silver iodide are of special interest as the silver halides are peculiar in their behaviour towards light.

Scholl<sup>1</sup> found that silver iodide, a poor conductor in the dark, became a much better conductor when illuminated. The wavelength most effective in producing the change in conductivity was  $\lambda 4330$ .

W. Wilson<sup>2</sup> studied the photo-electric effect and the increase in conductivity due to illumination in silver iodide simultaneously. With an arc lamp, the silver iodide was found to be ten times as active photo-electrically as an aluminium plate. The silver iodide was prepared by depositing a film of silver on a suitable plate and then converting it into the iodide by iodine vapour. The change in conductivity was produced both by violet and ultra-violet light, the effect due to the latter being only 8 to 10 % of that due to the former. The emission of photo-electrons only occurred when ultra-violet light was used. The absence of photo-electric effect in the violet might be attributed to the violet light penetrating to greater depths than the ultra-violet light, but this view cannot be correct according to the following observations. Wilson found the absorption coefficient of silver iodide (referred to 1 mm.) for the photo-electrically active rays to be 15,000. Scholl found the absorption coefficient of the rays most active in producing the increase in conductivity to be 13,000. Hence the explanation based on different penetrations is inadequate. [The coefficient denoted in optical works by  $nk$  is .44 for silver iodide. Drude gives 3.7 as the value corresponding to green light for silver.] It is somewhat surprising that the ultra-violet light produces a smaller conductivity change than the violet light. Wilson suggests the following explanation: Violet light causes

<sup>1</sup> Scholl, *Ann. d. Phys.* xvi. pp. 193, 417, 1905.

<sup>2</sup> W. Wilson, *Ann. d. Phys.* xxiii. p. 107, 1907.

the molecules to emit electrons with small velocities. These are easily directed by the applied electromotive force and so increase the conductivity. Ultra-violet light releases electrons of higher speed, which are less easily directed by the electromotive force, and hence the change in conductivity is less. In other words, the slow photo-electrons are more easily converted into free electrons, which determine the conductivity, than the faster photo-electrons.

Attempts to detect a change of conductivity in thin metallic films when exposed to light have yielded negative results because the free electrons are much more numerous than the photo-electrons produced (Bädeker<sup>1</sup>). This refers to continuous films. Wilson produced a film of granulated silver which was practically insulating. The tiny granules are probably separated by insulating air spaces and, in fact, the preparation is analogous to a fine-grain coherer. On illuminating the film by ultra-violet light, there was an increase of conductivity, which was independent of the potential applied. The conductivity in this case is produced only by light of the same wave-lengths as that which produces the photo-electric effect and not by light of longer wave-lengths in addition. Photo-electrons are probably emitted in all directions by the granules and the applied potential gives them a velocity component and hence the conductivity. When silver iodide was produced in a granulated layer like the granulated silver and not in a continuous layer as before, the conductivity effect again went together with the photo-electric effect. In the granulated materials, we are concerned with an emission of photo-electrons from a large number of surfaces within the substance, and hence it is only the light which produces a photo-electric effect that causes an increase in the conductivity.

### Liquids.

Brillouin<sup>2</sup> found that water was not photo-electric, while ice was. The author<sup>3</sup> found that when water was illuminated by the

<sup>1</sup> Bädeker, *Leipzig. Ber.* LV. p. 198, 1903.

<sup>2</sup> Brillouin, given in Sir J. J. Thomson, *Cond. Elec. through Gases*, p. 289.

<sup>3</sup> Hughes, *Phil. Mag.* xxiv. p. 380, 1912.

light from a mercury lamp, there was hardly any photo-electric effect at all.

Obolensky<sup>1</sup> has made some useful investigations on the photo-electric effect of ice, water and solutions. He used the light from a very powerful aluminium spark which was very rich in short wave-lengths. The light from this source was passed through several filters, given in the table. The quartz plate was 25 mm. thick and the calcite plate 3 mm. thick. In the second column the limit of transparency for the different substances (excepting calcite) is given from a consideration of Lyman's work (Chap. x). It is certain that the limit assigned to quartz by Obolensky, viz.  $\lambda 1850$ , is quite incorrect.

Light filter	Approximate short wave- length limit	Photo-electric effect		
		CuO	Ice	Water
I. Fluorite	$\lambda 1250$	100	100	100
II. Quartz	$\lambda 1450$	27	40	15
III. Quartz+air	$\lambda 1770$	22	50	11
IV. Calcite	$\lambda 2000$	<1	.02	0
V. Glass	$\lambda 3300$	0	0	0

We see that the Schumann region is most active in producing a photo-electric effect in water. Even thin quartz transmits only  $\frac{1}{6}$  of the active light, while calcite transmits none at all. The figures for cupric oxide, ice and water are not comparable with one another. The effects produced by the light passing through fluorite were 100, 70, and .25 in cupric oxide, ice and water respectively. Hence ice has a much bigger photo-electric effect than water, which confirms Brillouin's results. From an examination of the table it appears that the photo-electric effect in ice does not fall off so rapidly with increasing wave-length as the effect in water. Before building on these experiments, we should know what the penetrating power of light of short wave-length is in water and in ice. For if the light were absorbed in a thin layer in ice and in

<sup>1</sup> Obolensky, *Ann. d. Phys.* xxxix. p. 961, 1912.

a thicker layer in water, then relatively fewer photo-electrons would emerge from the water. There is no available information on this point. But, if we may disregard the '02 in the column for ice, the long wave-length limit is much the same for ice as for water.

From these results, it appears that there is a photo-electric effect in water with wave-lengths longer than  $\lambda 1770$ , but there is no effect with  $\lambda 2000$ . From the results of the author, we can perhaps get closer limits. Since the shortest wave-length in the mercury lamp cannot be said to produce any definite photo-electric effect, the photo-electric effect for water must set in between  $\lambda 1770$  and  $\lambda 1850$ . Oxygen is ionised only by wave-lengths less than  $\lambda 1350$ , while hydrogen has not been ionised at all. It is rather surprising therefore that water should be photo-electric with longer waves. Strictly speaking however, the effect should be compared for the gaseous state in all cases, or for the liquid state.

Traces of impurities do not produce any appreciable effect on the photo-electric properties of water.

With salt solutions, the following results were obtained. The light used was that transmitted through fluorite.

Concentration	NaCl	KCl	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>
0	100	100	100	100	100	100
2 %	85	35	325	156		
10 %	50	30	465	360	411	397
15 %	50	30	560	540		

The electro-negative ion in the salt appears to determine whether the effect increases or decreases. The chlorides all decrease the effect and it is well to note that the chlorine is the most electro-negative of the acid ions. Though the acid ions appear to determine the behaviour of the solution very largely, 20 % of sulphuric acid did not alter the effect of pure water. Experiments showed that the active spectral region is displaced somewhat to the ultra-violet for the chlorides and to the longer wave-lengths for the other salts.

In connection with these experiments on solutions, it is

convenient to refer to two experiments by the author<sup>1</sup>. It was found that zinc chloride and phosphorus pentoxide, sublimed in vacuo, had not the slightest trace of a photo-electric effect when the light from a mercury lamp was used. On admitting ordinary air for a time and then pumping it out, the surface of both substances became more or less wet. In this state, they had a big photo-electric effect, far larger than could be accounted for by the water effect (if any) with the wave-lengths available. It is difficult to see why a concentrated solution of zinc chloride or phosphorus pentoxide should be very much more photo-electric than either solute or solvent.

Before leaving this part of the subject, some remarks should be made on certain photo-electric experiments in which liquids are involved. Jaffé<sup>2</sup> found that an illuminated zinc plate immersed in hexane gave off negative electricity, the amount being of the order of one thousandth of that for zinc immersed in air in the ordinary way. Almost all the effect was due to the zinc, and no part of it could be definitely attributed to a volume effect in hexane.

More recently, Volmer<sup>3</sup> has shown that hexane is not ionised by the light from a mercury lamp. The experiments of Szivessy and Schäfer<sup>4</sup> on the ionisation of paraffin oil by ultra-violet light from a mercury lamp are inconclusive, and there was nothing to show that the effect found was not due (as in Jaffé's experiments) to photo-electric action of the light at the metallic electrodes.

### *Insulators.*

The results of a few miscellaneous experiments which can hardly be classified elsewhere are given here.

Reiger<sup>5</sup> investigated the photo-electric effect of a number of insulators, using an arc lamp as the source of light. Due care was taken to avoid spurious results arising from the charging up of the surface of these insulators. The photo-electric effect was small for the insulators tried, being much less than that for carbon.

<sup>1</sup> Hughes, *Phil. Mag.* xxiv. p. 380, 1912.

<sup>2</sup> Jaffé, *Phys. Zeits.* xi. p. 571, 1910.

<sup>3</sup> Volmer, *Ann. d. Phys.* xl. p. 775, 1913.

<sup>4</sup> Szivessy and Schäfer, *Ann. d. Phys.* xxxv. p. 511, 1911.

<sup>5</sup> Reiger, *Ann. d. Phys.* xvii. p. 935, 1905.

The following are relative values :

Ebonite	specimen 1	17·8
"	" 2	70·0
"	" 3	33·8
Mica		18·8
Sealing-wax		35·2
Beeswax		2·3
Resin		16·4

W. Wilson (*l.c.*) found that shellac had a photo-electric effect about  $\frac{1}{40}$  that of aluminium. Goldmann and Kalandyk (*l.c.*) also found that shellac was photo-electric. They found in addition that its conductivity increased when illuminated, showing, as in the case of sulphur, that photo-electrons were released in the substance. No permanent polarisation as a result of illumination could be obtained. Owing to its slight conductivity, shellac would not charge up permanently like sulphur. No appreciable photo-electric effect was shown by paraffin or by paraffin oil when illuminated by a mercury lamp.

## CHAPTER VIII

### PHOTO-ELECTRIC EFFECTS OF DYES, FLUORESCENT AND PHOSPHORESCENT SUBSTANCES

HALLWACHS<sup>1</sup> and Stoletow<sup>2</sup> were the first to show that a number of organic dyes were photo-electric when illuminated by light of short wave-length. Schmidt<sup>3</sup> concluded that there was no close connection between fluorescence and photo-electric effects. Fuchsine was found to be photo-electric when dissolved in water, but not when dissolved in alcohol, while both solutions are fluorescent. The explanation has been given by Rohde's experiments<sup>4</sup>. The reflecting power of a surface of a fresh aqueous solution of fuchsine or methyl violet increases with its age. In fact, a film of solid dye separates out, as can be shown by drawing a glass rod through the surface, on which a jagged tear is left. Rohde's method of recording the growth of the film was to suspend a sheet of metal in the solution of fuchsine or methyl violet by a fine wire. Torsion was gradually applied until the surface film was torn. The angle of torsion was a measure of the strength and thickness of the film. In Fig. 32, the ordinates represent the couple required to break films of methyl violet whose ages are given horizontally. The different curves refer to solutions of different concentrations. Now, the photo-electric effect of the solution also increased with the age, as is shown in Fig. 33. The similarity of the curves shows without any doubt that the photo-electric effect observed is that of the thin solid film of methyl violet which

<sup>1</sup> Hallwachs, *Wied. Ann.* xxxvii. p. 666, 1889.

<sup>2</sup> Stoletow, *Physikalische Revue*, Bd. i. 1892.

<sup>3</sup> Schmidt, *Ann. d. Phys.* LXIV. p. 708, 1898.

<sup>4</sup> Rohde, *Ann. d. Phys.* xix. p. 935, 1906.

separates out. There was no photo-electric effect with the alcoholic solution, neither was there any formation of a solid surface layer. Rohde found that solid fuchsine had much the

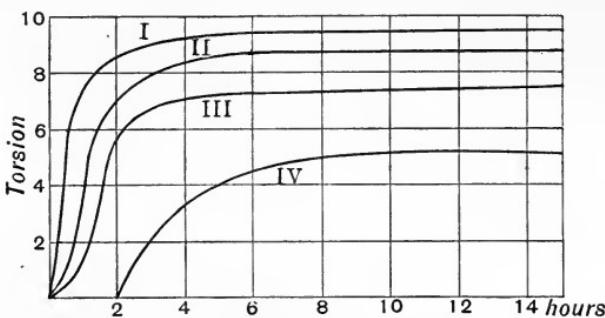


Fig. 32.

Formation of methyl violet film on water. Torsion experiments.

- I. 750 c.c. concentrated solution in  $\frac{3}{4}$  litre water.
- II. 375 c.c.      "      "      "
- III. 85 c.c.      "      "      "
- IV. 17 c.c.      "      "      "

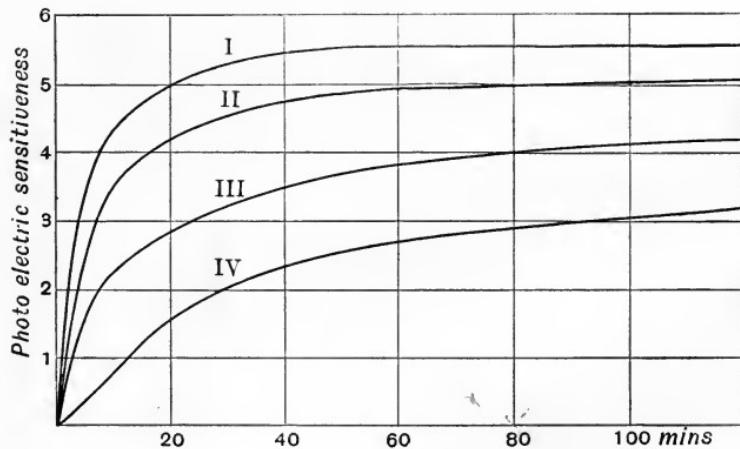


Fig. 33.

Formation of methyl violet film on water. Photo-electric experiments.

- I. 750 c.c. concentrated solution in  $\frac{3}{4}$  litre water.
- II. 375 c.c.      "      "      "
- III. 85 c.c.      "      "      "
- IV. 17 c.c.      "      "      "

same photo-electric effect as the layer on an old aqueous solution. The photo-electric effect of solid dyes depended to a considerable

extent on the degree of compactness of the dyes (see also Rohde's experiments on sulphides).

Stark and Steubing<sup>1</sup> investigated the photo-electric effect and fluorescence of a large number of organic substances. The photo-electric effect of some of the substances changed rapidly with exposure to the light (mercury lamp) owing to chemical changes produced by the light. In such cases, only the initial effect was taken as the real effect of that particular substance. The intensity of the fluorescence was given in five grades, arbitrarily estimated. A long table is given in the original paper containing the intensity of fluorescence and the magnitude of the photo-electric effect of the substances investigated. The authors conclude that, in general, the more intense the fluorescence, the greater the photo-electric effect, and consequently that the photo-electric effect and fluorescence in the organic substances investigated are fundamentally connected. An examination of their table does not carry conviction as to the justification for their conclusion. When we remember that very many substances show photo-electric effects with the source of light used, and that the photo-electric effect varies enormously with the state of the surface of any substance and depends upon the depth to which the light penetrates and other conditions, it is very doubtful, even if fluorescence and the photo-electric effect were fundamentally connected, whether a close connection would be shown in experiments of this kind. These considerations make it desirable to look for a relation between fluorescence and the photo-electric effect in a somewhat different way.

Pauli<sup>2</sup> adopted a method which possesses some novel features for investigating the problem. The ratio of the intensity of the fluorescent light to that of the exciting light was studied as a function of its relation to the wave-length of the exciting light. At the same time, the photo-electric effect was investigated. Now if there is a fundamental relation between the two effects, we should expect a marked photo-electric effect with the most active exciting light. Organic fluorescent solids were laid on a

<sup>1</sup> Stark and Steubing, *Phys. Zeits.* ix. p. 481, 1908.

<sup>2</sup> Pauli, *Ann. d. Phys.* xl. p. 677, 1913.

shallow tray which was connected to the electrometer. Around this tray was a cylindrical electrode, which could be raised to any desired potential. On illuminating these fluorescent substances they all showed very marked actino-dielectric effects (see p. 108). A typical case is given in Fig. 34 for eosine. The two curves give the progress of the leak with the time, the cylinder being at a positive or negative potential relative to the illuminated substance. After a time the actino-dielectric effect disappears, leaving the photo-electric effect, provided the field is favourable to the escape of negative electricity. The actino-dielectric effect is independent

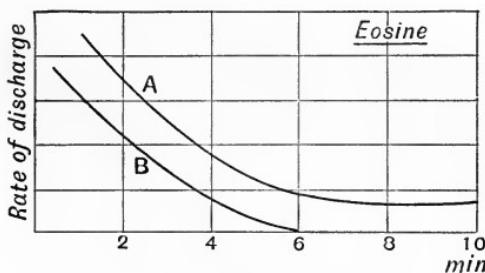


Fig. 34.

- A. Surrounding cylinder at + potential.
- B. " " " - potential.

of the direction of the field. Taking a zinc plate as a standard of reference and calling its photo-electric effect 2000, the most active fluorescent substance was anthracene with 10, and the least active eosine with 1.2. On plotting the intensity of the actino-dielectric

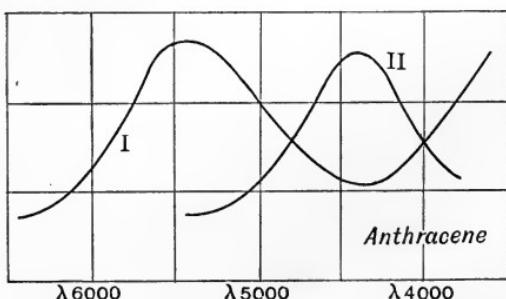


Fig. 35.

- I. Actino-dielectric effect.
- II. Efficiency of light for exciting fluorescence.

effect and the efficiency of the exciting light against the wave-length, no relation at all was shown between the light exciting fluorescence and that producing the actino-dielectric effect. For anthracene, the maximum for the former was at  $\lambda 4450$ , for the latter at  $\lambda 5400$  (Fig. 35). In Fig. 36 we have sets of three curves. Curve I gives the distribution of the fluorescent light, curve II the efficiency of the exciting light, and curve III the magnitude of the photo-electric effect. In no case did visible light produce a photo-electric effect, while in all the substances chosen the light most efficient in stimulating fluorescence was in the green or blue. Moreover, the photo-electric effect always increases with decreasing

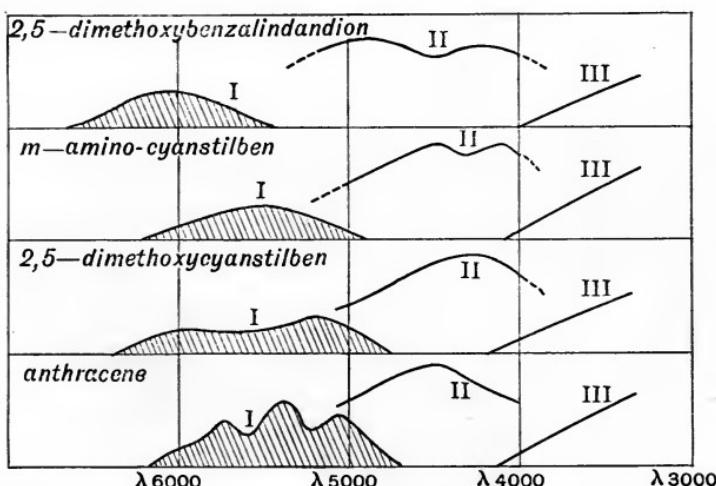


Fig. 36.

wave-length, while the shape of curve II for the exciting light is characteristic of the particular substance investigated. Hence there appears to be no connection between the fluorescence of a substance and its photo-electric effect.

Byk and Borck<sup>1</sup> and Pochettino<sup>2</sup> have observed a photo-electric effect in anthracene. The former devised a new method to overcome the difficulty met with in their experiments by the high insulating power of anthracene. Pochettino applied the term "fatigue" to the falling off of the photo-electric effect of

<sup>1</sup> Byk and Borck, *Verh. d. Deutsch. Phys. Ges.* xii. p. 621, 1910.

<sup>2</sup> Pochettino, *Accad. Lincei, Atti*, xv. p. 355, 1906.

anthracene during exposure to light. It is better to avoid the use of the term in this connection, as fatigue in anthracene is quite a different thing from fatigue in metals. The so-called fatigue in anthracene is merely due to its insulating properties, which cause it to charge up until its potential becomes almost equal to that of the opposing electrode, and then the photo-electric current ceases.

The author<sup>1</sup> found that a layer of anthracene, distilled in vacuo, gave off electrons when illuminated by the light from a mercury lamp. The velocities of the photo-electrons were in agreement with the law which has been established for metals,

$$V = kn - V_0.$$

The critical wave-length at which the effect sets in for anthracene is between  $\lambda 2150$  and  $\lambda 2200$ . That  $k$  is of the same order for anthracene as for the metals points to the identity of the photo-electric process, whether in metals or in organic bodies of very different chemical constitution. In fact (excepting Pohl and Pringsheim's selective effect for the alkali metals) the only characteristic in the photo-electric effect which depends on the substance used is the long wave-length limit.

Stark looked for an increased conductivity in a fluorescing solution of anthracene in benzol and in hexane, but with negative results. Volmer<sup>2</sup> has obtained some useful results from experiments on anthracene dissolved in hexane. He also confirmed the result given above, that anthracene in vacuo does not give off photo-electrons unless it is illuminated by wave-lengths shorter than  $\lambda 2250$ . Before commencing the experiments on solutions of anthracene the hexane was repeatedly purified until its conductivity in the dark and due to illumination became negligible. Then any small effect due to the conductivity of the illuminated solution of anthracene could be detected and attributed to the dissolved anthracene. An arc lamp was used in these experiments. In Volmer's experiments on the conductivity of illuminated anthracene solutions there appear to be two distinct effects. One

<sup>1</sup> Hughes, *Phil. Mag.* xxiv. p. 380, 1912.

<sup>2</sup> Volmer, *Ann. d. Phys.* xl. p. 775, 1913.

is a direct photo-electric effect and the other is a conductivity apparently arising out of a photo-chemical process in which the anthracene splits up into positive and negative ions. With wave-lengths longer than  $\lambda 2250$  there is no trace of a conductivity due to a *volume* ionisation of the fluorescing anthracene solution. But when the solution is saturated, and only then, a conductivity due to illumination appears, which was traced to an effect localized at the thin layers of precipitated anthracene at the electrodes. Volmer suggests that some anthracene molecules are split up by the light into positive and negative ions which go into solution and follow the electric field. [Note.—A similar experiment was tried with sulphur, which is only slightly soluble in hexane. Evidence was obtained that, in this case, only the positive ions went into solution.] Light of wave-length longer than  $\lambda 2250$  was also found to increase the conductivity of solid anthracene, but did not produce a photo-electric effect. It may repay investigation to examine whether there is any further connection between the conductivity produced in solid anthracene by wave-lengths longer than  $\lambda 2250$  and this new effect in illuminated solutions.

When, however, wave-lengths shorter than  $\lambda 2250$  are used, the solution is found to acquire a conductivity due to volume ionisation. Probably photo-electrons are emitted from the anthracene molecules and become negative ions leaving a positive anthracene molecule. (This view could be tested by mobility experiments, for the negative ion would be a molecule or cluster of molecules of the solvent only, while the positive ion necessarily contains an anthracene molecule.) With these short wave-lengths the slightest trace of anthracene in the hexane produces a very marked increase in the conductivity on illumination, the order being 100—300 times. The conductivity is directly proportional to the amount of liquid illuminated. As the potential difference increases, the current becomes almost saturated between 320 and 640 volts. The maximum conductivity occurs, in the particular form of cell used, when the concentration of the anthracene is .00025 normal. Greater concentrations caused the light to be completely absorbed in too thin a layer close to the window.

Other substances dissolved in hexane were tested and the volume ionisation measured. The results are given in the

following table, together with Stark's relative values for the photo-electric effect of the solid substances.

Substance	Conductivity of solution	Relative photo-electric effect for solute
Naphthalene	0	1·2
Phenol	0	2·2
Phenanthrene	6	8·2
Diphenylmethane	7	17·0
$\beta$ -Phenol	10	10·6
Anthracene	20	12·5
$\alpha$ -Naphthylamine	40	15·0
Diphenylamine	50	17·0

It is clear that the increased volume conductivity of a solution is very closely connected with the photo-electric effect of the corresponding solute. This was also checked by using absorption screens for the light. The two effects for anthracene, solid and in solution, went together. The anthracene molecule, when suitably illuminated, loses an electron, this electron sticks to the nearest neutral molecule, and thus we get the necessary conditions for the conductivity.

The region producing fluorescence in anthracene,  $\lambda 4000 - \lambda 2250$ , does not produce photo-electric effects. The results of Volmer's experiments, in addition to those of Pauli, Schmidt, and Rohde on fluorescent organic bodies, and those of Henry, Whiddington and Franck and Westphal on fluorescing iodine vapour, give us strong grounds for concluding that the electron disturbance associated with fluorescence has nothing to do with the photo-electric effect. It seems very unlikely that anthracene vapour is ionised by light of wave-lengths greater than  $\lambda 2200$  (the limit for solid anthracene), but quite a long range, extending to the visible, produces a fluorescence.

Stark<sup>1</sup> has shown that, in a number of cases, the benzene derivatives possess two absorption bands with which fluorescence bands are associated. In most cases, the long wave-length band only has been shown to exist, but analogy suggests that other fluorescent benzene derivatives also possess a short wave-length absorption band far in the ultra-violet. The fluorescence usually

<sup>1</sup> Stark, *Phys. Zeits.* ix. p. 481, 1908; *Ann. d. Phys.* xli. p. 728, 1913.

observed is excited when light belonging to the long wave-length absorption band is absorbed and is, as we have seen, unaccompanied by photo-electric effects. When light belonging to the short wave-length absorption band falls on the substance, it appears, from the evidence available, that a photo-electric effect is produced as well as fluorescence.

Fluorescence does not seem to involve the separation of an electron from its parent molecule, for in the cases given above the fluorescence is often most marked when there is no trace of any photo-electric effect or any conductivity indicating the separation of electrons. It appears as if the disturbing light causes the electron to be displaced within the sphere of influence of the molecule, and that the fluorescent light is due to the electron settling down to its equilibrium position. The experiments of Franck and Westphal indicate that it is easier to separate an electron from a fluorescing molecule than from a non-fluorescing molecule.

There are a number of processes produced by light which, like fluorescence, do not necessarily involve any separation of electricity which can be detected by our methods. Such processes are the formation of ozone from oxygen by ultra-violet light, the combination of hydrogen and chlorine when suitably illuminated, and the decomposition of water vapour by light.

The increased conductivity of alcoholic solutions of dyes when illuminated has been investigated by Goldmann<sup>1</sup>. It was found that there was no increase in the conductivity itself, but that an electromotive force (about 2 volt) was produced in a capillary layer of the dye solution bounded by an electrode. The electromotive force was independent of the light intensity, in which respect it behaves similarly to the emission velocities of photo-electrons. The light used was limited to the visible spectrum. This effect is probably similar to that investigated by Volmer for the longer wavelengths.

#### *Phosphorescent Substances.*

Lenard and Saeland<sup>2</sup> have made an extensive examination of the photo-electric properties of a certain class of phosphorescent

<sup>1</sup> Goldmann, *Ann. d. Phys.* xxvii. p. 449, 1908.

<sup>2</sup> Lenard and Saeland, *Ann. d. Phys.* xxviii. p. 476, 1909.

bodies. These substances, which were previously studied by Lenard and Klatt<sup>1</sup>, consist of a sulphide of Ca, Sr or Ba, a trace of an added metal such as Bi, Ni or Pb, and a flux such as  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{B}_4\text{O}_7$ , which are all fused together. Such a substance, called a "phosphor," is very phosphorescent. The photo-electric activity differs very much between different "phosphors," and even the same one may have its activity altered very much by imperceptible surface changes. The most active one, calcium sulphide, with bismuth as the added metal, gave nearly as big a photo-electric effect as freshly polished magnesium. The maximum emission velocity did not exceed that corresponding to 2 volts. These substances are good insulators, and so they show the actino-dielectric effect which is only apparent during the first few minutes of illumination. The surface charges up positively until no further emission of photo-electrons takes place. It was found that when the surface ceases to emit any more electrons, only  $\frac{1}{10}$ th of the surface was really charged. This justifies the authors in considering that the photo-electric effect is not distributed over the surface, but is localized in those "centres" which are active in a phosphorescent sense. Previous investigations had led Lenard to associate phosphorescence with active "centres" rather than with the whole mass of the substance. The close connection between the photo-electric effect and the phosphorescent effect was established in this way. Both effects were tested in

- (1) pure sulphide,
- (2) added metal,
- (3) the flux,

and in combinations of these two by two. The phosphorescence and the photo-electric effect were only well marked in the combination of the three constituents.

By using coloured glasses as light filters it was established that the light which did not produce phosphorescence did not produce the photo-electric effect. The view given is that electrons leave the "centres" and become embedded in the surrounding insulating medium. The phosphorescence is produced by the electrons falling

<sup>1</sup> Lenard and Klatt, *Ann. d. Phys.* xv. p. 671, 1904.

back into the polarised centres. The duration of the phosphorescence is determined by the insulation of the medium, which in turn depends on the temperature. When the insulation is poor the electrons fall into the polarised "centres" quickly and give a short duration phosphorescence, and conversely. When the "centres" are on the surface they may lose some of their electrons outwards, giving rise to a photo-electric effect. The nature of the phosphorescent light is determined by the disturbances produced when the electrons fall into the "centres," and not by the character of the exciting light. The photo-electric effect ceases immediately with the cutting off of the light, and hence it is associated with the ejection of electrons and not with their return to the "centres." In other words, the photo-electric effect is not connected with the *intensity* of the phosphorescence, but with the *excitation* of the phosphorescence.

Butman<sup>1</sup> finds that there is a well-marked photo-electric effect in the CaBiNa "phosphor" (i.e. CaS + Bi + Na flux), and that this effect requires wave-lengths less than  $\lambda 4100$  to produce it. The maximum emission velocity does not exceed that corresponding to .35 volt. It is also stated that sulphur is photo-electric to wave-lengths longer than  $\lambda 3200$ . (This is not in agreement with Goldmann and Kalandyk's results.) Hence Butman concludes that the photo-electric effect of the "phosphor" is associated with that of the sulphur in it. The light which does not produce phosphorescence does not produce the photo-electric effect. This statement does not appear to have been sufficiently tested. It was found that the light from an arc lamp passed through red, yellow or green glass did not produce either effect. To establish this statement on a more exact basis it is certainly desirable to carry out the tests using narrow bands in the ultra-violet, and to investigate whether those wave-lengths which are particularly active in stimulating phosphorescence produce a big photo-electric effect.

The difference between fluorescence and phosphorescence appears to be this. In phosphorescence, the electrons get away beyond the sphere of influence of the "centre," and as an electron returns to a polarised "centre" an emission of light occurs whose

<sup>1</sup> Butman, *Phys. Rev.* xxxiv. pp. 158, 316, 1912; *Amer. Jour. Sci.* xxxiv. p. 133, 1912.

period is determined by the disturbance produced as the electron settles down to its equilibrium position in the "centre." Hence, if the "centres" lie on the surface, the electron may get away completely, giving a photo-electric effect. In fluorescence, the electron is disturbed but does not get away beyond the sphere of influence, and in settling down to its equilibrium position the fluorescent light is emitted.

These views are in harmony with the fact that a photo-electric effect accompanies phosphorescence but does not as a rule accompany fluorescence.

## CHAPTER IX

### POSITIVE RAYS PRODUCED BY LIGHT

NUMEROUS as are the difficulties which require attention in experiments on photo-electric effects, the complication arising from the emission of positively charged particles, along with the photo-electrons from an illuminated plate, has fortunately never been a source of trouble. It has been tacitly assumed all along that an illuminated plate does not emit positive electricity, and the existence of a positive current has never been suggested, directly or indirectly, by experiments on other aspects of photo-electricity. We should, however, call attention to the interesting experiments of Dember<sup>1</sup>, which point to the emission of a very feeble current of positive rays along with the much more copious stream of electrons.

The apparatus is shown in Fig. 37. *A* is a thick metal plate which is perforated near the centre by a number of narrow channels ( $\approx 1$  mm. diameter). *B* is a Faraday cylinder surrounding the receiving plate *C*, which is connected to an electrometer. *D* is a piece of gauze which serves as anode. When *D* is at a positive potential relative to *A*, the photo-electrons leaving *A* are all drawn into the gauze and the current is measured by the galvanometer *G*. But simultaneously *C* acquires a positive charge of a much smaller order of magnitude. The positive charge can arise in two ways. The electrons leaving *A* and accelerated towards *D* produce ions by collision. The positive ions so produced will be directed towards *A* by the field, and some of them will go through the channels and yield up their charges to *C*. If we assume that positive particles are emitted by *A* in addition to photo-electrons,

<sup>1</sup> Dember, *Ann. d. Phys.* xxx. p. 142, 1910.

then these positive particles will start off towards *D*, but will be forced back to *A* in parabolic paths by the electric field and some will pass through the channels. These two effects can be separated by studying the way in which the current varies with the potential difference between *A* and *D* at different pressures. The curve in Fig. 38, giving the positive charge acquired by *C*, was obtained when the residual gas was at a pressure of  $\cdot 0008$  mm. It is quite evident that ionisation of the gaseous molecules by collision sets in when the potential difference becomes greater than 10 volts. On reducing the distance between *A* and *D* to 2 mm., and the pressure to a value below  $\cdot 00001$  mm., the curves in Fig. 39 were obtained. The Cu and Au refer to the illuminated metal. We see that the current is nearly constant from 10 volts to 40 volts; so

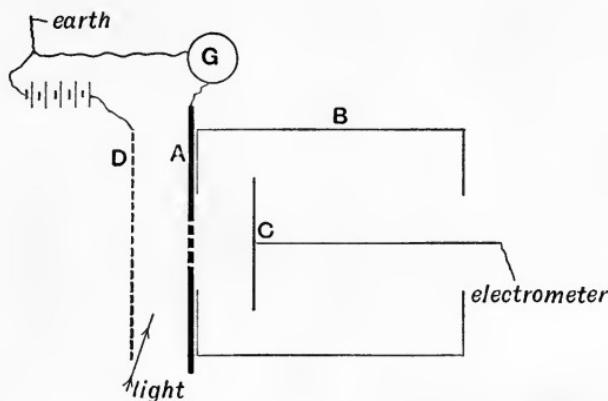


Fig. 37.

evidently no positive ions are produced by collisions of the photo-electrons with gaseous molecules between *A* and *D*. It might be suggested that some stray light finds its way to *C* and causes it to lose electrons, thereby becoming positively charged. But changing the field between *A* and *D* from 0 volt to 1 volt and to 40 volts should have no effect on the emission of electrons from *C*. Dember therefore concludes that positively charged particles leave the illuminated surface *A* and are compelled by the field to return towards it, some of them penetrating through the channels. On this view, the curves in Fig. 39 indicate that the maximum emission energies of these positive particles correspond to a voltage of from 4 to 6. This value for the maximum energy appeared

to remain unchanged as the light intensity increased from 1 to 1.8. Using a zinc plate with a very large number of channels (68 holes each 1 mm. diameter), the positive current to *C* was  $3 \times 10^{-13}$  amp., while the negative current to *D* was  $3.7 \times 10^{-9}$  amp.

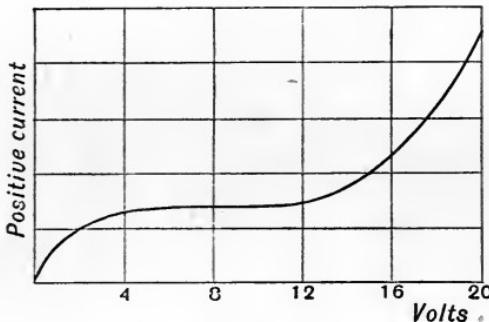


Fig. 38.  
Magnesium .0008 mm. air.

This very large ratio of the negative current (photo-electrons) to the positive current probably explains why the positive current does not interfere with the usual photo-electric experiments.

It is somewhat strange that this effect has not been investigated further since its discovery was announced. It seems desirable to extend the investigation in various directions and to

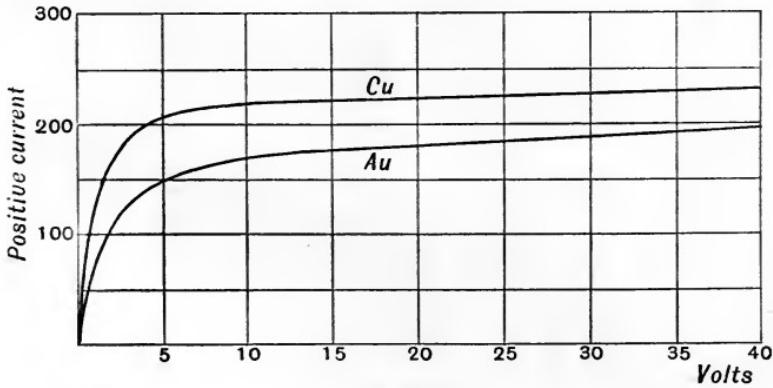


Fig. 39.

see how the emission of the positive particles depends on the different factors, such as the frequency and intensity of the light and the nature of the illuminated surface. A measurement of the ratio  $e/m$  for the positive rays from different metallic surfaces should tell us something about their origin.

## CHAPTER X

### SOURCES OF LIGHT USED IN PHOTO-ELECTRIC EXPERIMENTS

As a knowledge of the wave-lengths used in different photo-electric experiments is of great importance in interpreting the results, it will be useful to give in conclusion a short account of the sources of light most generally used in such experiments.

A. The most useful source of ultra-violet light for general purposes is the mercury lamp, a convenient form of which is

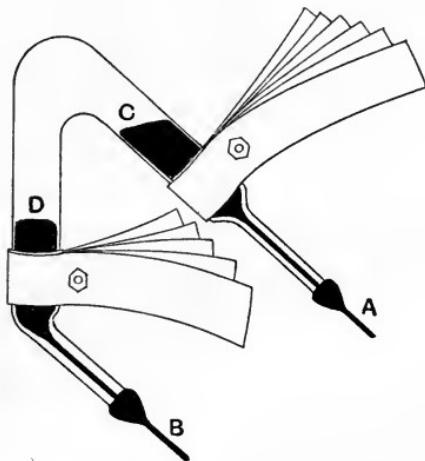


Fig. 40.

shown in Fig. 40. It consists of a tube of quartz glass (clear fused silica) about 1 cm. in diameter, exhausted as completely as possible. Sufficient mercury is put into the tube beforehand, so that on tilting it an electric current can flow from A to B through liquid mercury. On bringing the lamp back again to its normal vertical position, the column of mercury breaks and a brilliant arc flashes

out between *C* and *D*. Copper radiators are generally fixed outside the quartz tube to convey the heat away from the electrodes, and so the lamp is kept comparatively cool. The electric current through the lamp is at first large, but after 10 or 20 minutes it drops to its final value and then the emission of light becomes remarkably constant. The constancy of the emission of light, its great intensity, and the fact that the lamp once started needs no attention whatever, account for the popularity of the lamp as a source of ultra-violet light. The voltage generally used for mercury lamps is between 50 and 200 volts and the current is from 3 to 5 amperes. The ultra-violet light from the mercury lamp and other powerful sources produces painful effects in the eyes when they are exposed to it for any length of time. It is therefore advisable to enclose the lamp in a box so arranged that the light can be transmitted only into the photo-electric apparatus. The spectrum of the mercury arc in vacuo consists of a large number of bright lines extending from about  $\lambda 2300$  to  $\lambda 5790$ . A useful list of the more intense lines is given by Arons<sup>1</sup>. The line  $\lambda 2540$  is particularly effective in producing photo-electrons from most metals, because of its great intensity and its situation well in the ultra-violet. A number of very weak lines are found below  $\lambda 2000$ , the shortest being  $\lambda 1849$ . These lines do not show up readily in photographs of the spectrum of the mercury arc. Nevertheless, they are of great importance in experiments on emission velocities of photo-electrons (Chapter III). The mercury arc itself emits light of still shorter wave-length, which however is absorbed by the quartz glass of the lamp.

B. Electric sparks, produced by an induction coil between various metallic terminals, with a condenser in parallel, are frequently used as sources of ultra-violet light. Their disadvantage lies in the fact that it is extremely difficult to keep them steady. On the other hand, they emit light of shorter wave-lengths and of greater intensity than the mercury lamp. The spark between aluminium terminals gives very powerful lines at  $\lambda 1852$ ,  $\lambda 1864$ ,  $\lambda 1935$ , and  $\lambda 1990$ . Still shorter wave-lengths are recorded by Morris Airy<sup>2</sup> at  $\lambda 1785$ ,  $\lambda 1741$ ,  $\lambda 1709$ , and  $\lambda 1693$ , and also by

<sup>1</sup> Arons, *Ann. d. Phys.* xxiii. p. 176, 1905.

<sup>2</sup> Morris Airy, *Manchester Lit. and Phil. Soc.* xlvi. p. 1, 1905.

Lyman<sup>1</sup>. Lenard<sup>2</sup> has described a source of ultra-violet light of very great power. A short spark between aluminium terminals is produced by a big induction coil, the primary of which takes 90 amperes. The condenser in parallel with the spark has a capacity of .11 microfarad. The rate at which energy is given out by such a spark exceeds 1000 watts, which is greater than the power of many carbon arcs. Such a source is very rich indeed in light of short wave-lengths. Lyman<sup>3</sup> gives a list of wave-lengths down to  $\lambda 1239$  for the light emitted by a bright aluminium spark, which however was much less intense than Lenard's spark.

C. The discharge in hydrogen at a pressure of 1 to 5 mm. is extremely rich in light of very short wave-length. A large number of lines between  $\lambda 1030$  and  $\lambda 1650$  has been recorded by Lyman<sup>4</sup>. Such a discharge is very feeble to the eye compared with the intense light from a mercury lamp. Yet Hull and St John<sup>5</sup> found that the light from such a discharge in hydrogen, when passed through a fluorite plate, produced a photo-electric effect at a zinc plate 250 times greater than that produced by a mercury lamp. The reason for this is that the hydrogen discharge emits far more energy in the extreme ultra-violet than does the mercury lamp.

D. The ordinary carbon arc has occasionally been used as a source of ultra-violet light. The intensity of the ultra-violet spectrum falls off rapidly, being inappreciable beyond  $\lambda 2400$ .

### *Transparency Limits of different Substances.*

The source of light has in most cases to be separated from the experimental chamber by some air-tight transparent window, and its transparency limit (that is, the shortest wave-length which it transmits) should be known in addition to the spectral range of the source. Lyman's investigations<sup>6</sup> of the transparencies of

<sup>1</sup> Lyman, *Astrophysical Journal*, xxxv. p. 341, 1912.

<sup>2</sup> Lenard, *Sitzungsberichte d. Heid. Akad. d. Wissen.* 1910.

<sup>3</sup> Lyman, *Astrophysical Journal*, xxxv. p. 341, 1912.

<sup>4</sup> Lyman, *Astrophysical Journal*, xxiii. p. 181, 1906.

<sup>5</sup> Hull and St John, *Phys. Rev.* (2), i. p. 329, 1913.

<sup>6</sup> Lyman, *Astrophysical Journal*, xxv. p. 45, 1907.

various substances are most useful for our purpose. Clear colourless fluorite is the most transparent substance known. The best specimens (1 to 2 mm. thick) transmit as far as  $\lambda 1250$ .

Plates of crystalline quartz, in thickness of about 2 mm., transmit to  $\lambda 1450$ , of 2 mm. to  $\lambda 1500$ , and of 20 mm. to  $\lambda 1600$ . Rock salt (2 mm. thick) is less transparent, the limit being  $\lambda 1770$ . The author tested the transparency of clear quartz glass (or fused silica). The plate, which was 3 or 4 mm. thick, transmitted 24% of  $\lambda 1849$ , 36% of  $\lambda 1971$ , and 40% of  $\lambda 2002$ . The very rapid increase in opacity explains why  $\lambda 1849$  is the shortest wavelength emitted by an ordinary mercury lamp made of quartz glass. Common soda glass, 2 or 3 mm. thick, transmits to about  $\lambda 3300$ . When considerably thinner, say 2 mm. or less, it may easily transmit as far as  $\lambda 2500$ . Mica, even in the thinnest sheets, has sharply defined transparency limits, which vary a little with the specimen of mica but are usually near to  $\lambda 3000$ .

A column of water 1 cm. long cuts out all wave-lengths shorter than  $\lambda 2200$ .

Many of the common gases absorb strongly in the extreme ultra-violet, frequently termed the Schumann region. We are indebted to Lyman<sup>1</sup> for exact information about the absorption of gases in this region. The gases were all tested in a cell 91 cm. long. Hydrogen is quite transparent. Nitrogen (760 mm.) shows only a very slight absorption, which increases regularly with decreasing wave-length, though even at  $\lambda 1250$  the absorption is very small. Oxygen has an absorption band which broadens unsymmetrically with increasing pressure. At atmospheric pressure it extends from  $\lambda 1270$  to  $\lambda 1760$ , at 40 mm. from  $\lambda 1330$  to  $\lambda 1600$ , and at 15 mm. from  $\lambda 1350$  to  $\lambda 1500$ . Carbon monoxide has eight narrow absorption bands between  $\lambda 1250$  and  $\lambda 1600$ . Carbon dioxide has a broad band like that of oxygen, the position of the more refrangible end being unknown. The absorption of air is similar to that of oxygen, though under like conditions the air band is slightly narrower than the oxygen band.

I have investigated the short wave-length limit of a number of quartz and fluorite plates, using the maximum emission velocities of photo-electrons as an indication of the shortest wave-length

<sup>1</sup> Lyman, *Astrophysical Journal*, xxvii. p. 87, 1908.

transmitted. There was little or no variation in the transparency of the quartz plates (approximately 3 mm. thick), but the variations in the transparency of clear colourless fluorite were extraordinary. Out of thirty or more specimens, not more than five transmitted further than quartz, and many of the others were considerably worse than quartz. Two specimens (from different sources) of perfectly clear colourless fluorite supplied by Zeiss had approximately  $\lambda 1330$  and  $\lambda 1700$  as their respective limits. Hence it is unjustifiable to assume that the transparency of fluorite is the same as that of Lyman's best specimens. Each piece should be tested separately, and it is not easy to do this spectroscopically as the vacuum spectroscope which is necessary is not usually available. It seems, however, that we can rely on plates of quartz 2 or 3 mm. thick transmitting down to  $\lambda 1450$ , and plates 2 mm. thick transmitting to  $\lambda 1500$ . Lenard<sup>1</sup> assigns to crystalline quartz a transparency limit  $\lambda 1800$  and to quartz glass  $\lambda 2200$ . In view of Lyman's direct measurements on crystalline quartz, this seems doubtful; it is well to remember this when considering Lenard's experiments. I have obtained  $\lambda 1849$  from mercury lamps of quartz glass, the thickness of the tube being about 5 to 1 mm. It should be remembered that in photo-electric experiments the effects produced increase very rapidly with decreasing wave-lengths, and wave-lengths which are too weak to give any photographic record spectroscopically without special precautions may play the most important part in a photo-electric experiment. For example, anthracene, when illuminated by the light from a mercury lamp, is photo-electrically active, and direct measurements show that only light of wave-length shorter than  $\lambda 2200$  is effective. But lines of shorter wave-length than this do not appear on the photographs of the mercury arc spectrum unless long exposures are given.

On considering the above data, we arrive at the following conclusions. The shortest wave-length emitted by the ordinary mercury lamp is  $\lambda 1849$ . The shortest wave-length emitted by a hydrogen discharge through a fluorite window may be  $\lambda 1250$  if the fluorite is of the best quality. The fluorite should be tested for transparency. If a thin quartz window (< 5 mm. thick) be

<sup>1</sup> Lenard, *Sitzungsberichte d. Heid. Akad. d. Wissen.* p. 35, November, 1910.

used instead, the limit may be assumed to be  $\lambda 1450$ . Should the light be then transmitted through a centimetre of oxygen or air, the limits are shifted to  $\lambda 1770$  and  $\lambda 1710$  respectively. If, instead of quartz, fluorite is used with the oxygen column, a narrow band would be emitted between  $\lambda 1250$  and  $\lambda 1270$ , in addition to the wave-lengths longer than  $\lambda 1770$ , if the fluorite is of the best quality. Very little is known of the emission from sparks in the short wave-length region, but assuming that no wide gaps exist in the emission spectra, then the shortest wave-length is determined approximately by the transparency limits of the fluorite, quartz, air, or other medium through which the light passes. Lyman<sup>1</sup> gives a list of a number of aluminium spark lines below  $\lambda 1700$ . The aluminium spark in air emits a group of strong lines near  $\lambda 1300$ , and these are very effective in ionising air.

### Light Filters.

To isolate any required region of the spectrum, a monochromator is most useful. The instruments now available are not designed to isolate wave-lengths shorter than  $\lambda 1849$ . Light filters can often be used instead of a monochromator with advantage, but their use is limited to wave-lengths longer than  $\lambda 3000$ , as no substance is known to exhibit a selective transmission beyond this wave-length. Lists of light filters are given in R. W. Wood's *Physical Optics*, in a paper by Luther and Forbes<sup>2</sup>, and in other papers. I have found the following filters useful in isolating the mercury lines:

- $\lambda 5790$  and  $\lambda 5770$ . Wratten and Wainwright's yellow filter, No. 22.
- $\lambda 5461$ . Wratten and Wainwright's green filter, No. 62.
- $\lambda 4360$ . Separate solutions of potassium permanganate and nickel nitrate, of just sufficient concentration to cut out other lines.
- $\lambda 3650$ . Nitrosodimethylaniline and methyl violet transmit  $\lambda 3650$  and  $\lambda 3340$ . The  $\lambda 3340$  was cut out by a thick block of glass.

<sup>1</sup> Lyman, *Astrophysical Journal*, xxxv. p. 341, 1912.

<sup>2</sup> Luther and Forbes, *Jour. Chem. Soc.* xxxi. p. 770, 1909.

$\lambda 3130$ . R. W. Wood recommends a silver film deposited on quartz. Unless the film is so thick as to reduce the intensity of  $\lambda 3130$  very considerably, many of the other lines appear as well. I found that a certain sheet of white mica transmitted  $\lambda 3130$  almost entirely, and was opaque to  $\lambda 3027$  and shorter wave-lengths. Thus we can get a sharp limit on the ultra-violet side of  $\lambda 3130$ . This may be useful in cases when the presence of other lines longer than  $\lambda 3130$  makes but little difference.

Winther<sup>1</sup> gives a list of ultra-violet filters, which are said to transmit from 30% to 40% of the selected lines. These filters should be very useful provided that the intensity of the light of other wave-lengths is reduced to such an extent that its effects are negligible.

<sup>1</sup> Winther, *Zeits. f. Elektrochem.* xix. p. 389, 1913.

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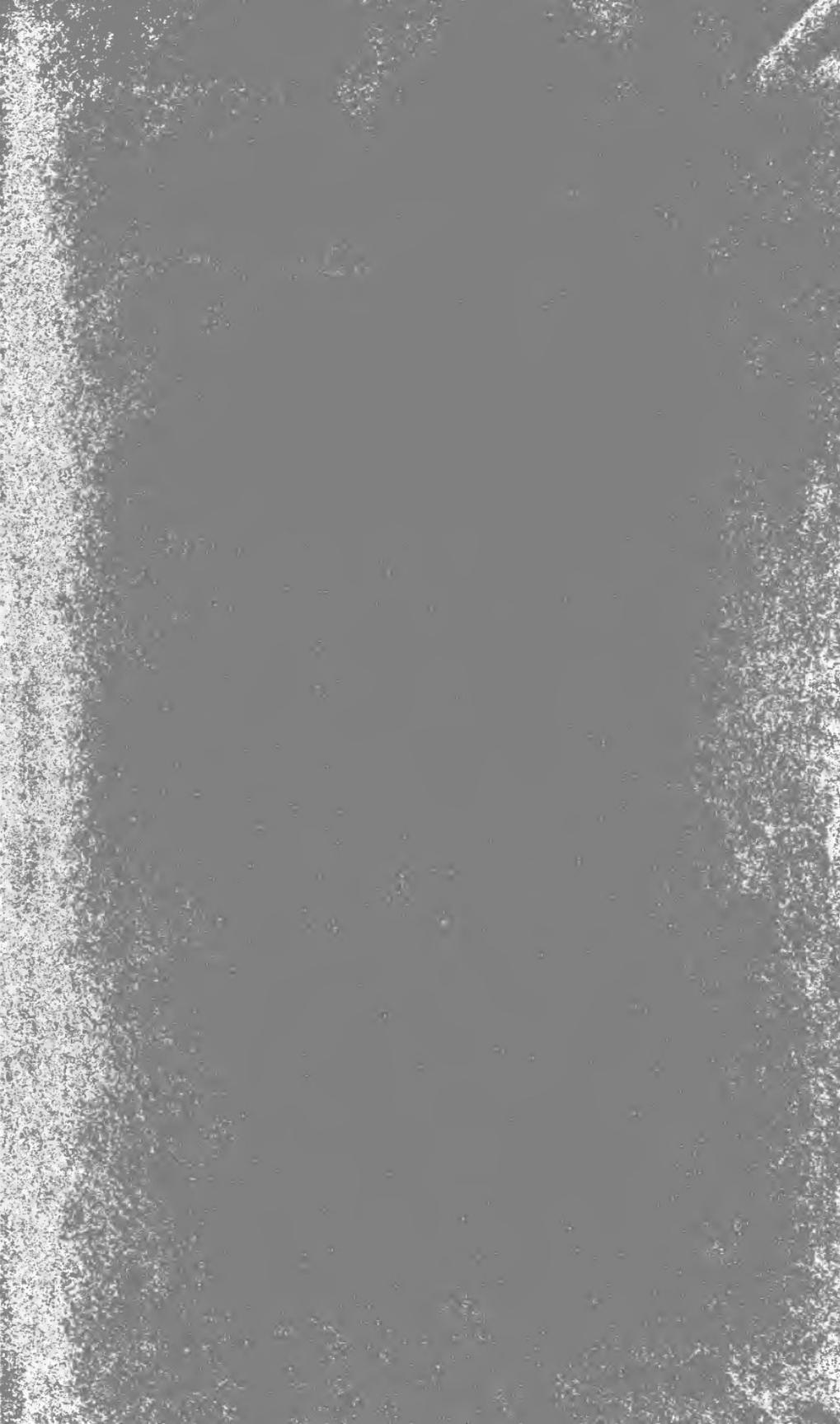
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